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## **Paper recycling : recovery of secondary fibers by selective wettability**

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PAPER RECYCLING:  
RECOVERY OF SECONDARY FIBERS BY SELECTIVE WETTABILITY  
BY  
GARY KEITH WELSHANS

A DISSERTATION  
PRESENTED IN PARTIAL FULFILLMENT OF  
THE REQUIREMENTS FOR THE DEGREE  
OF  
DOCTOR OF ENGINEERING SCIENCE  
AT  
NEW JERSEY INSTITUTE OF TECHNOLOGY

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Newark, New Jersey  
1978

## ABSTRACT

A separation process has been developed which recovers similar paper grades from a mixed stock by selective wettability. This process capitalizes on the various paper additives which are intended to resist water wetting and result in paper flotation. While water can be used to achieve many desirable paper separations, the detention times required are excessive, and therefore, limit any industrial application. Surface-active agents, in low concentrations, can be used advantageously by reducing the detention times for all paper while the structure of the surfactant can be used to selectively recover similar papers over a controlled time period. Detention times have been established with several ionic and non-ionic surfactants over various concentration ranges. The surface and capillary wetting processes have been determined for a number of different commercial grades including catalog, foodboard, kraft shipping sacks, and others. The governing parameters which were found to retard quiescent water wetting included fiber surface charge, coatings, chemical pulping, sizing agents, wet-strength additives, and basis weights. While all surfactants accelerate paper wetting, the charge of the surfactant is critical in determining a desirable separation scheme. In low concentrations, cationic surfactants effectively separate bleached from unbleached papers; anionic surfactants lowered the detention times of unbleached kraft papers when separated from bleached kraft papers. While non-ionic surfactants accelerate all paper wetting, they are non-specific in separations. From measurements made on the transmittance of cationic surfactants through bleached papers, the surface spreading coefficients were found to be

proportional to the detention times. Consequently, at a specific surfactant level the liquid penetrates the pores dispelling the entrapped air so that different grades wet and sink at distinctly different times readily allowing separation. A dynamic batch plant system has been studied which significantly increases the through-put that can be achieved under quiescent settling conditions. It was found that neither paper size nor paper shape had any appreciable effect on the detention times when using this recovery process. Lower detention times could be achieved by increasing surfactant concentrations, the mixing agitation, and the power input, or by reducing the loading rates. This paper recovery process can be used in secondary fiber operations to achieve higher fiber yields resulting in a savings of labor and virgin timber, and a reduction in the solid waste problem.

APPROVAL OF DISSERTATION

PAPER RECYCLING:

RECOVERY OF SECONDARY FIBERS BY SELECTIVE WETTABILITY

BY

GARY KEITH WELSHANS

FOR

DEPARTMENT OF CIVIL AND ENVIRONMENTAL ENGINEERING

NEW JERSEY INSTITUTE OF TECHNOLOGY

BY

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NEWARK, NEW JERSEY

MAY, 1978

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Gary K. Welshans

This dissertation is  
dedicated to  
my loving parents

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## I INTRODUCTION

The ever-increasing consumption of paper products, accompanying rises in pulp costs, and concern about ecology are resulting in a wider interest in secondary fiber pulps. The complex problem of reuse results from the difficulties of gathering the wastepaper from scattered sources, sorting the various grades from the mixed stock, which is usually done by hand, and recovering the fiber from the many types of paper products.<sup>(1)</sup>

As a component of solid waste, paper comprises approximately one-third by weight of all disposed municipal refuse. Table 1 shows the distribution of the major paper categories for the year 1972.<sup>(2)</sup> The largest category of wastepaper is corrugated containers which comprise 28.8 percent of all discarded papers. Newspapers represent 19.5 percent as do the combined printing and writing papers. Packaging and miscellaneous papers make up the remaining 32.2 percent. One can also see that roughly 53 percent of these products are generated from residences while the remainder are discarded from commercial or institutional sources. While representing 50 percent of the total paper usage, residential newspapers, commercial corrugated boxes, and printing and writing papers from offices are the most easily recoverable grades and

| <u>Product Category</u> | <u>Paper Discards</u><br><u>1,000 tons</u> | <u>Percent</u> | <u>%</u><br><u>Residential</u><br><u>Generated</u> | <u>%</u><br><u>Commercial and</u><br><u>Institutional</u><br><u>Discards</u> |
|-------------------------|--|----------------|--|--|
| Newspapers              | 9,600                                      | 19.5           | 89.6   | 10.4   |
| Corrugated Boxes        | 14,100                                     | 28.8           | 15.5   | 84.5   |
| Printing and Writing    | 9,600                                      | 19.5           | 57.3   | 42.7   |
| Packaging and Other     | 15,800                                     | 32.2           | 61.4   | 38.6   |
| Total                   | 49,100                                     | 100.0          | 53.0   | 47.0   |

TABLE 1. GENERATION OF PAPER BY COMPONENT AND SOURCE, 1972

source of secondary fiber because of the relative ease of concentration and separation.

The United States currently consumes more than 60 million tons of paper and paperboard annually of which only about 20 percent are recycled.<sup>(3)</sup> In 1974, the American Paper Institute estimated that 14.2 million tons of secondary fiber were provided, supplying 22 percent of the industry's requirement, when the total of manufactured paper products reached 64.2 million tons. The economic recession of 1975 caused a decline of total paper consumption by 13.5 percent of the previous year. During this period the consumption of wastepaper showed a similar decline of 17 percent.

Table 2 shows, in thousands of tons, the weight of wastepaper recycled and projected annually for 1970 to 1978. The data through 1975 are based on actual consumption; the data for the years 1976 to 1978 were estimated by the American Paper Institute's Capacity Survey of secondary fiber mill managers.<sup>(3)</sup> Table 3 was compiled for the actual consumption of wastepaper for 1972 based on whether the recovered paper was generated from industrial converting operations or from the waste stream of the final customers.<sup>(2)</sup> While industrial converters recycle 80 to 90 percent of their wastes, post-consumers, in general, recycle only about 15 percent of their wastepapers.

These tables list the four main categories of wastepaper: printed newspapers, old corrugated boxes, mixed papers, and high-grades. In general, the newspapers are derived from newsstands and home collection

|                                | <u>1970</u> | <u>1971</u> | <u>1972</u> | <u>1973</u> | <u>1974</u> | <u>1975</u> | <u>1976</u> | <u>1977</u> | <u>1978</u> |
|--------------------------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|
| Total                          | 12,021      | 12,323      | 13,132      | 14,318      | 14,196      | 11,630      | 15,646      | 16,035      | 16,240      |
| Newspapers                     | 2,235       | 2,174       | 2,317       | 2,578       | 2,408       | 2,045       | 2,633       | 2,674       | 2,697       |
| Used Corrugated<br>Boxes       | 4,080       | 4,277       | 4,722       | 5,292       | 5,716       | 4,480       | 6,528       | 6,751       | 6,851       |
| Mixed Papers                   | 2,639       | 2,776       | 3,054       | 3,251       | 3,118       | 2,568       | 3,295       | 3,345       | 3,368       |
| Pulp Substitutes<br>High-Grade | 3,067       | 3,097       | 3,037       | 3,199       | 2,955       | 2,537       | 3,189       | 3,265       | 3,335       |

Table compiled April, 1976

TABLE 2. WASTE PAPERS RECYCLED (THOUSAND TONS)

| <u>Grade Category</u>          | <u>Converted Waste</u> | <u>Post-Consumer Waste</u> | <u>Total</u> |
|--------------------------------|------------------------|----------------------------|--------------|
| Newspapers                     | 280                    | 2,037                      | 2,317        |
| Used Corrugated Boxes          | 1,650                  | 3,072                      | 4,722        |
| Mixed Papers                   | 886                    | 2,168                      | 3,054        |
| Pulp Substitutes<br>High-Grade | 2,383                  | 654                        | 3,037        |
| Total                          | 5,199                  | 7,931                      | 13,130       |

TABLE 3. WASTE PAPERS RECYCLED, 1972 (THOUSAND TONS)

drives conducted by the Boy Scouts, schools, or other community groups. While 22 percent of old newspapers were recycled in 1974, over 8.3 million tons were discarded as solid waste. Approximately 90 percent of old newspapers are generated from residences and households where it is relatively easy to separate newspapers from other household wastes. The U. S. Environmental Protection Agency estimates that more than 134 communities make special provisions to conduct separate collection programs where adequate secondary-fiber markets exist.<sup>(4)</sup>

Nearly 85 percent of all used corrugated boxes originate from commercial and industrial establishments where they can be easily separated at the source.<sup>(5)</sup> While they comprise over 35 percent of all the recycled papers, about 11 million tons are not collected annually. Favorable market conditions encourage supermarkets, warehouses, and retail stores to recover this category of paper.

Mixed papers, which come from waste baskets of office buildings, institutions, and similar sources, have little economic value because of the high amount of contaminating materials and its heterogeneous nature. Although printing and writing paper represents only 20 percent of all paper discards, approximately 43 percent of this fiber can be found in the mixed waste generated from office or commercial sources. Stationery and office papers separated from the mixed papers have high economic values.<sup>(6)</sup>

The last category of wastepaper, the high-grade stock, accumulates mainly from envelope and printing plants as rejects or trimmings. Used magazines are returned from newsstands or from residences. These grades

can be hand sorted from mixed office wastes. They have a high economic value with a market that has remained stable over the past several years.

The major end uses for each of the four wastepaper grade categories can be seen in Table 4.<sup>(4)</sup> The highest end use is found in the manufacture of recycled board which is used for such items as cereal, detergent, and shoe boxes. Other areas which are dependent upon wastepapers include tissues, printing and writing, and construction products. Very little reclaimed fiber goes into the production of unbleached kraft packaging paper and of bleached and unbleached kraft board.

Figure 1 shows the relative importance of wood pulp to paper stock for the majority of papers produced in 1967.<sup>(7)</sup> The shaded areas indicate the relative amount of virgin pulp used for each of the paper grades, while the white areas indicate the relative amount of recycled wastepapers used.

Papers consume 51.7 percent of the virgin pulp and 13.4 percent of wastepapers, while comprising 44.0 percent of the total industry production. Recycled paper only amounts to 6.6 percent of newsprint, writing, packaging, and tissue papers.

The paperboard segment consumes 43.0 percent of the virgin pulp and 79.4 percent of wastepapers, while comprising 47.9 percent of the total output. Secondary fibers compose over a third of the material needed for this diverse grade.

| End Use                         | Total<br>Production | Total<br>Waste Paper | Grade Category |       |       |            |
|---------------------------------|---------------------|----------------------|----------------|-------|-------|------------|
|                                 |                     |                      | News           | Corr. | Mixed | High-Grade |
| Total Paper                     | 26,750              | 2,870                | 594            | 140   | 317   | 1,938      |
| Newsprint                       | 3,430               | 490                  | 482            | ---   | 17    | ---        |
| Printing & Writing              | 13,500              | 938                  | ---            | ---   | 44    | 893        |
| Unbleached Kraft Pkg.           | 5,840               | 263                  | 14             | 15    | 47    | 187        |
| Tissue                          | 3,980               | 1,179                | 98             | 125   | 98    | 858        |
| Total Paperboard                | 29,570              | 9,858                | 1,657          | 4,916 | 2,136 | 1,151      |
| Unbl. & Bl. Kraft               | 17,430              | 449                  | 1              | 355   | 50    | 44         |
| Semichemical                    | 4,260               | 849                  | 19             | 747   | 77    | 7          |
| Recycled                        | 7,880               | 8,560                | 1,637          | 3,814 | 2,009 | 1,100      |
| Construction Paper<br>and Board | 5,700               | 1,591                | 327            | 235   | 919   | 109        |
| Total                           | 62,020              | 14,439               | 2,578          | 5,292 | 3,371 | 3,199      |
| Percent                         |                     | 100                  | 17.2           | 37.0  | 23.5  | 22.3       |

TABLE 4. END USES FOR WASTE PAPER, BY GRADE OF WASTE PAPER USED, 1973 (THOUSAND TONS)



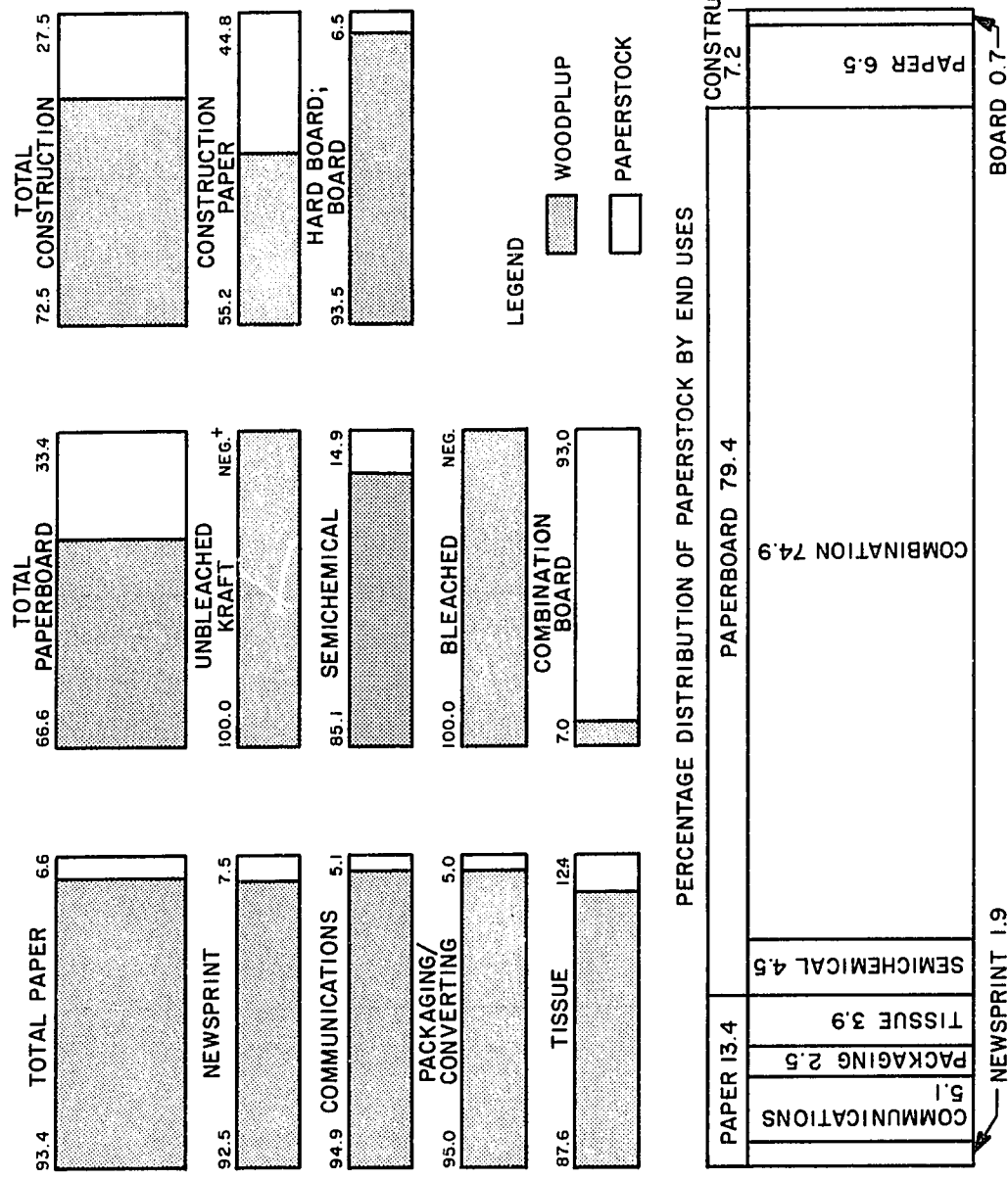


FIGURE 1. RELATIVE IMPORTANCE OF WOODPULP AND PAPERSTOCK TO MAJOR GRADES PRODUCED, 1967

The construction area uses 5.3 percent of virgin material and 7.2 percent of the recycled papers, while comprising 8.1 percent of the production. Wastepapers account for 27.5 percent of the raw material used in this area.

While there are more than 12,000 kinds of paper produced for more than 100,000 specific end uses, they can be classified on the basis of their pulp formation.<sup>(8,9,10,11,12)</sup> Groundwood pulps are mechanically produced by grinding to separate the fiber from the binders. They contain all the chemical components of wood, such as lignin, hemicellulose, and resin. The fibers are relatively short with little strength. Because of their good opacity and bulkiness these papers have good printing qualities and are used extensively for newsprint and writing papers.

The sulfite, or acid, pulp uses sulfurous acid to separate the cellulose fibers from the wood. The paper produced by this method is used mostly in the printing grades, or business papers, and into sanitary tissues.<sup>(13)</sup>

The most important method to produce paper comes from the kraft, or sulfate, pulp. Sodium sulfide along with caustic soda are used to manufacture the cheapest and strongest fibers. These durable fibers are used principally in paperboard, coarse grades, packaging, printing and tissues.

The last major process to produce paper comes from semichemical pulp. Using chemical and mechanical separation of the wood fibers, the

finished products are used predominantly for the corrugated medium in paperboard boxes and, to a lesser degree, for inexpensive printing papers. Other natural fibers, other than wood and synthetic fibers, are also used in the paper industry.

While chlorine or chlorine dioxide can be used to bleach and brighten the paper sheets, usually additives, coatings, or sizes are applied to make the product desirable for a specific end use. The chemical additives are added during the preparation of the fibers, or later, in either the drying phase or during a separate operation. The additives are used to improve a deficient paper property by improving its strength, increasing the degree of water resistance, affecting optical and printing qualities, or by reducing production problems.

While our current recycling rate is only 22 percent, there are many who believe the rate will sharply increase. Our current recycling level is well below that of 1919 when wastepaper was 28 percent of the total fiber and that of the peak of World War II when paper drives resulted in a 36-percent recycling rate. It is worth noting that recycling ranges from the low 30-percent levels in developed countries, such as France, Germany, and the United Kingdom, to 40-percent and 42-percent levels in Japan and the Netherlands, respectively.<sup>(14,15)</sup>

Also, there are several environmental and economic factors which can drive the level of secondary fiber, as a percentage of total paper produced, to those achieved in other countries where virgin pulp is relatively scarce. One of these factors lies in the area of solid-waste handling.

Many of our communities are rapidly filling up their cheap disposal sites.<sup>(16)</sup> They are faced with modern antipollution statutes which make it too expensive to expand operating landfills or to continue operating many incinerators. The economic value for paper and other resources has spurned the planning of several recycling plants. New York State, for instance, has plans for 21 of these plants to operate by 1985 which will be able to recycle almost half of the state's solid waste.<sup>(17)</sup> Besides the ecological costs, rising costs of resources and energy will lead to better solid-waste management programs and higher recycling rates of many now discarded items.

Another important factor which should lead to increase our waste-paper recycling levels is associated with the virgin-timber resources and the paper industries dependent upon them. Economic and environmental regulations have resulted in the closing of about 500 paper plants since 1960.<sup>(18)</sup> There are about 6,000 plants still in operation but pollution control laws have limited the potential new sites to a handful. Pollution controls have added about 25 percent to the cost of a new plant. It is anticipated that the equipment necessary to abide by the 1983 and 1985 water pollution standards will result in more plant closings. The paper industry's past practices of clear-cutting, razing the mountainside causing mudslides, and depleting wilderness areas have become national issues. More than one-third of our country's 254 million acres of public forested lands cannot be harvested because they are classified as park, wilderness, or rec-

recreation areas. A recent forestry act has restricted the industry from clearcutting in all the national forests. As a result the demand for private forests has increased dramatically in the past five years so that the price of prime timberland has risen from \$200 to \$800 per acre. The environmental and economic factors facing the paper industry should increase wastepaper recycling and result in the construction of several new paper recycling plants. They can be located in urban centers because they operate at relatively low levels of pollution and energy and transportation costs can be reduced. Furthermore, for each ton of recycled paper it is estimated that this paper saves 17 trees,<sup>(19)</sup> so that at the present rate of recycling we are saving approximately 275 million trees per year.

The last important area of consideration is connected to the energy savings and pollution reductions when recycled materials are used rather than virgin materials. With an increase in wastepaper recycling, more virgin timber could be used to increase the supply of wood in construction and reduce the wood substitutes such as steel floor joists and aluminum framing for exterior walls which require fifty and twenty times as much energy for production as wood, respectively.<sup>(3)</sup> Over 15 percent of our petroleum is used to produce synthetic materials. From wood it is now possible to manufacture ethylene, chlorine, vanilla, acetone, butanol, and glucose. If more wood could be directed in these areas, a savings of oil would result. Energy can be saved in the production of recycled papers which requires 25 percent less energy than those papers manufactured from trees. This savings is equivalent to one-quarter of a pound of coal or 3,000 BTU's per pound of

recycled paper produced. While paper in garbage generally has a higher heating value than the other combustibles, most power plants are not volume-limited or weight-limited, but are BTU-limited. Consequently, if the paper has been removed, more combustible garbage can become available for incineration to increase the solid-waste disposal. Also, waste newspapers have a higher economic value for recycling than they have for fuel. As a fuel wastepaper is half the cost of coal or one-third the cost of oil. In addition, recycling can reduce the dependency on imported paper which amounts to seven million tons of newsprint annually.<sup>(20)</sup>

All of the reasons considered in this brief overview are creating a situation which will improve the market for recycled wastepaper. Besides the action of the federal government to recover office papers, newspapers, and corrugated containers from all their major establishments, citizen and governmental officials are contemplating specific changes in public policies. These include proposals to revise tax policies and transportation rate structures regarding virgin and recycled materials, place waste charges on all paper products entering the waste stream, and modify governmental procurement policies to require purchasing recycled materials instead of virgin products.

Future levels of wastepaper recycling are very much in doubt. A report published in 1973 by the Midwest Research Institute for the American Paper Institute projected that the recycling rate could decline to 17 percent by 1985 if there was an absence of external forces on the industry.<sup>(21)</sup> They concluded that demand from customers and

public policy changes could result in a 26 percent recycling level in 1985. At this rate they estimated that 25.8 million tons of wastepaper would be recycled in that year. Recycling rates greater than 35 percent are used by the National Academy of Sciences while government reports state goals of 50 percent recycling by that time.

In order to achieve these high recycling rates, it is generally agreed that source separation of papers from other wastes must be more fully used. Again, the areas of greatest concern lie in the collection of bundled newspapers from residences, corrugated containers from commercial establishments, and the separation of high-grade office paper. While computer tab cards and print-outs have recently been separated at their source because of their high resale value, the process by which other high-grade pulp substitutes can be extracted from mixed office papers has received little attention.

Techniques employing hand sorting have changed very little since 1920.<sup>(22)</sup> Besides removing trash and contaminants associated with the mixed paper such as plastic cups, soda cans, and garbage, wastepaper dealers must use manual labor to identify and sort 45 different grades recognized by the Paper Stock Institute. Some dealers have as many as 65 classifications for his paper stock, but most smaller dealers do not find it economically feasible to sort more than a dozen grades. If very pure separations can be achieved, the paper mills can take advantage of using the secondary fiber as direct pulp substitutes in many cases. Practical and economic restraints on the salvage operations frequently prevent the separation of high-grade from the mixed

paper.

A large waste sorting operation requires a large plant, conveyor belts or elevators, materials handling equipment, and baling presses.<sup>(23)</sup>

In a typical vertical processing plant consisting of three stories, the incoming bales of potentially high-grade stock are delivered on the third floor where they are opened, separated into various classes, and put in chutes leading to the second floor. The second floor is equipped with a conveyor belt leading to all of the various bins of separated papers. When a specific grade is desired, the papers from the appropriate bin are placed on the conveyor belt and moved to an opening in the floor above a hopper located on the first floor. After dropping into the hopper, the papers are baled and sent to a pulper requesting this grade of fiber. A similar separation can be achieved using a horizontal processing operation which relies on conveyors running throughout the plant rather than the use of gravity.

While land costs usually dictate the structure of the operation, the quantities of materials that can be hand picked from mixed waste are very close. It has been estimated that between 1.5 and 3.0 tons of papers can be sorted per person per day.<sup>(22)</sup> The total operating costs, including the physical acquisition of concentrated wastepaper, the hand sorting and baling are estimated to be between \$9 and \$15 per ton. The values of waste papers can range from a low of \$5 to \$10 per ton of mixed papers when the market has little demand to \$200 or more per ton for the relatively pure high-grade pulp substitutes.

New technology is being developed to help solve the sorting pro-



blem. One of the most promising advanced techniques receiving particular interest is being demonstrated by the Black Clawson Fiberclaim process under a grant by the U.S. Environment Protection Agency.<sup>(24,25)</sup> This demonstration project is located in Franklin, Ohio, and is designed to process municipal refuse while producing metals, glass, and fibrous materials. The pilot plant has a design capacity of 150 tons per day with 20 percent yields of usable paper fiber, 9 percent ferrous metal, 4 percent glass, and 0.3 percent aluminum. The remaining organics which are not reclaimable are incinerated in a fluidized bed reactor. After the Hydropulper wet grinds the incoming refuse, a liquid cyclone extracts the glass into a fiber recovery system where a low-grade of paper fiber is recovered. This product is a combination of newspapers, corrugated, and mixed papers and is consequently equivalent to mixed paper. It is used locally to make felt paper for asphalt roofing shingles. EPA has published dubiously high prices for their paper fiber ranging from \$25 to \$65 per ton as delivered in a slurry pipeline.

Other methods used to separate and recover waste paper from mixed wastes employ a dry air classification process.<sup>(26)</sup> The Stanford Research Institute located in Irvine, California, subjects shredded materials in an upward flowing zig-zag air column. Heavy materials which can not be supported in the air stream fall to the bottom and the light fractions of plastics and Styrofoam are ejected at the top. Their process is extremely dependent upon the density and aerodynamic differences between the materials to be separated. Because of the amount of dirt, entrained glass, and other particulate material car-

ried through to the paper fraction, the polluted papers must be further subjected to extensive cleaning. One paper company has suggested that this process "might preferably serve as an adjunct or pre-processing step to some other system as one of its early stages."

The Forest Products Laboratory in Madison, Wisconsin, is developing a combination dry and wet separation system.<sup>(22)</sup> The paper fraction is supplied by a cooperating agency which has initially hammer-milled and air separated the papers from mixed waste. The laboratory screens this product to get its starting material and then subjects it to a Hydropulper similar to that used by Black Clawson's Fiberclaim process. By adjusting the screens, this system was designed to obtain five grades which included newspapers, corrugated, magazines, unbleached, and all other paper. The deficiency in this process lies in upgrading the fiber properties. When the fibers are upgraded from the mixed paper category, the overall yield is reduced so that not all of the fibers can be efficiently used resulting in serious economic problems.

Wastepapers have also been removed from mixed wastes at several resource recovery demonstration projects financed in part by the U.S. Environmental Protection Agency. They are generally used for their fuel value and are not recycled into secondary paper products. The cities of St. Louis, Mo., and Wilmington, Del., shred the waste for fuel and recover the noncombustible materials. Pyrolysis is used by San Diego County, Ca., and Baltimore, Md., to produce fuel oil and steam generation as well as the noncombustibles. The city of Lowell,

Mass., incinerates its refuse leaving a residue which can be mechanically segregated and recovered.<sup>(27)</sup> The Franklin Institute in Philadelphia, Pa., and Sickson Paper Fibers, Inc., are developing a ballistic separator to mechanically separate mixed papers from other shredded refuse.

There are a number of resource research and development projects under way in Europe.<sup>(28)</sup> Because of the materials found in European municipal solid waste, their recovery objectives generally stress paper recovery. A Berlin contractor is designing a mechanical system to manufacture a paper similar to kraft which can be applied to separate collections from household and office wastepaper. The Warren Spring Laboratory, England, is recovering about 20 percent of air-classified paper with plastic contaminants. The Imperial-Krauss-Maffer Industrieanlagen, in Munich use screens to recover papers which contain about 5 percent plastics and other contraries. Esmil-Habets and a Dutch government laboratory in Haarlem use two zig-zag air classifiers to recover the paper fraction from plastics and metals. A Swedish firm using air-handling equipment and pulp dryers reports that their process can separate newspaper from corrugated, chipboard, and other packaging materials still contaminated with plastics and cellophane.

While new technology is being explored to recover more paper fibers from the waste stream, the finished reclaimed material fall into a low grade for reuse. Only hand sorting can be relied upon to effectively recover the high-grade pulp substitutes from concentrated

mixed wastes. These newer processes, while designed to operate on municipal and office wastes, contain high amounts of groundwoods and other impurities which limit their usefulness.

The impurities found in the lower grades of mixed papers include carbon papers, waxed papers, impregnated paper, glassine, parchment, bits of clothing, typewriter ribbons, woodchips, dirt, heavily covered posters, and wet-strength papers.<sup>(29)</sup> Other materials which must be removed include string, asphalt, glass, staples, and rubber to achieve quality secondary paper usage. Groundwoods in excess of 10 percent are usually difficult to deink and bleach. Wet-strength papers are objectionable in large quantities because they resist fiber separation. Rubber and plastics in small quantities can ruin hundreds of tons of pulp. Some resin-coated and pigment-coated papers present difficult recovery problems with respect to the chemicals needed for treatment. There are many classifications of wastepaper depending upon the quantity and type of prohibitive materials and out-throws permitted in the various grades.

Because the many additives and coatings found in paper resist water wetting, some of the important ones should be mentioned.<sup>(30)</sup> Table 5 indicates some of the most frequently encountered additives and a brief description as to their uses. Rosin sizing improves the resistance to wetting by water and improves the writing quality of ink. Starches and animal glues also resist wetting as well as add to improving properties such as paper strength, smoothness, and printability. They are also used extensively as the adhesive in the fabri-

| Chemical Additive                       | Uses   |
|---|--|
| Rosin                                   | Internal Sizing                                |
| Starches (corn, potato, tapioca, wheat) | Improved strength, corrugating, surface sizing |
| Animal glue                             | Surface sizing                                 |
| Urea-formaldehyde resin                 | Wet strength                                   |
| Melamine-formaldehyde resin             | Wet strength                                   |
| Polyamide resin                         | Wet strength, filler retention                 |
| Clay (Kaolin)                           | Coating, filler                                |
| Surfactants                             | Absorbency, wetting                            |
| Pigments                                | Improve paper coloring                         |
| Resins (vinyl, styrene, acrylic)        | Coatings                                       |
| Waxes                                   | Sizing, coating                                |
| Slimacides                              | Production problems                            |
| Defoamers                               | Production problems                            |

TABLE 5. COMMON BEATER ADDITIVES USED BY THE PAPER INDUSTRY

cation of corrugated box boards. Urea-formaldehyde, melamine-formaldehyde, and polyamide resins are used in waterproofing and to increase the wet-strength property of paper. The large consumption of white clays, usually Kaolin, fills the fiber surface voids, which results in a smooth surface which improves brightness, opacity, and the printing characteristics of the paper. Surface-active agents insure absorbency when incorporated with paper towels. Pigments, which are also frequently added to paper, include talc, titanium dioxide, calcium carbonate, and colored pigments which improve opacity and brightness, softness, and ink absorption properties. Various resins, waxes, and gums coat the papers and improve some other characteristic. Slime-cides and defoamers help during the production operations to combat specific problems. There are still many other ingredients which are added for other, specific end-use category products.

The presence of most of these additives results in paper stock which has a high resistance to water penetration. Consequently, while cellulose and most of the other components in paper have a specific gravity greater than 1.00, the pore spaces between the fibers, which are filled with air, will cause individual paper sheets to float for some finite time on a water surface.

It is the purpose of this investigation to study a novel process which can be employed in paper reclamation and recycling to increase the high-grade fraction from mixed papers. This process will be based on a wet-separation technique utilizing the fact that most papers contain coatings and other additives which tend to resist water wetting

causing them to remain floating over a specific time period. It is anticipated that surfactants, or detergents, in small concentrations can be used advantageously to control and accelerate the wetting and sinking times of similar papers so that high recovery rates can be achieved on the more valuable fiber fractions.<sup>(31)</sup>

Because surfactants in low concentrations have been used to wet the papers, a brief discussion of them is appropriate. Surface-active agents, or surfactants, are synthetic detergents which began mainly as substitutes for fat-based soaps in the late 1920's and early 1930's but developed into sophisticated products, and are superior in many respects to soap. The paper industry has found many uses for these compounds due to the lowering of surface tension, which assist in the properties of wetting, detergency, foaming, and emulsifying. More specifically, they promote penetration of the cooking liquor into the chips, retard the natural loss of absorbency due to aging, and, as already mentioned, work as rewetting agents in absorbent papers. Surfactants are used as emulsifying agents in pitch removal and control. They have been found to be of great assistance in the dinking process of secondary papers while appreciably removing dirt, ink, and fillers.

While surfactants are not primarily manufactured for the paper industry, they are used by them in many ways.<sup>(32,33,34,35,36,37)</sup> Water-soluble surfactants have been found to be excellent wetting agents in the paper, textile, and related fiber industries. Surfactants have been used by these industries as anti-static agents, fiber lubricants, and as dispersants. An excellent list of detergents and emul-

sifiers commercially available can be found in McCutcheon's Handbook, Allured Publishing Corporation.<sup>(38)</sup>

Table 6 shows a simplified representation of some typical surfactant models. A brief analysis of the chemical structure of the surfactants will reveal two essential parts. One end of the molecule has a hydrophillic, or water-soluble radical, which is repelled by waxes and other nonpolar substances. The other end, which repels water, has hydrophobic properties, and is attracted by fats, oils, and nonpolar substances. In general, the hydrophobic part of the molecule attaches itself to the solid, or fiber, and the hydrophillic end attaches itself to the water molecule.<sup>(39)</sup>

There are three distinct classes of surfactants which can be distinguished, and, naturally, many more possibilities exist within a class depending upon a balance of the hydrophillic and hydrophobic ends. Anionic detergents produce electrically negative ions in solution. Cationics produce electrically positive colloidal ions. Non-ionics are electrically neutral in solution. Amphoteric detergents can act as either anionic or cationic detergents depending upon the pH of the solution.<sup>(40)</sup>

Cationics are primarily used as emulsifiers, anti-static agents, and lubricants.<sup>(41)</sup> Anionics are particularly effective as foam stabilizers, emulsifiers, and as penetrating agents. Non-ionic surfactants have found industrial uses as lubricants, emulsifiers, dispersants, and dye leveling agents.



| Hydrophobic group<br>(Non polar)       | Hydrophilic group<br>(Polar)                    | Class    | Name                             |
|--|---|----------|----------------------------------|
| (-) $\text{CH}_3\text{CH}_2\text{---}$ | $\text{CH}_2\text{COON}_a$ (+)                  | Anionic  | Soap                             |
| (+) $\text{CH}_3\text{CH}_2\text{---}$ | $\text{CH}_2\text{HR}_3\text{Br}$ (-)           | Cationic | Quaternary ammonium salt         |
| $\text{CH}_3\text{CH}_2\text{---}$     | $\text{CH}(\text{OCH}_2\text{CH}_2)_n\text{OH}$ | Nonionic | Polyethylene-oxide<br>derivative |

TABLE 6. ABBREVIATED STRUCTURES FOR SURFACE-ACTIVE AGENTS

Commercial sizing agents provide the fiber surface with relatively low surface energy coating in order that high-energy aqueous liquids will be discouraged from moving extensively on the cellulose surfaces.<sup>(42)</sup> The orientation of the amphipathic molecules is vitally important to provide the low-energy monolayer on the pulp fiber surface. It is desirable for the paper manufacturer to have the hydrophobic layer of the surfactants firmly attached to the cellulose surface for maximum water repelency using minimum amounts of sizing agents.

Although surfactants have never been used to preferentially wet and separate high-grades of paper, they are used in the normal treatment of secondary pulps. The most common deinking processes used on wastepapers require heavy doses of alkalies such as caustic soda, soda ash, or sodium phosphates, while using surfactants as wetting agents and detergents.<sup>(43)</sup> Typical pulping conditions for making deinked stock for yellow pad paper require 1.5 to 2 percent NaOH and 0.5 percent soap.<sup>(23)</sup> To process books and magazines another recipe calls for 3.0 percent NaOH and 0.5 percent synthetic detergent. There are other applications of detergents in the paper recycling field. Besides removing ink they are used to remove coating and impregnants in the wash. The desired concentration levels are patented and are not readily available. A flotation process is sometimes used to remove contaminants from the pulp formed in secondary recovery operations. To remove the contaminants as a froth or scum in flotation machines, a typical formulation recommends 1.7% soft soap while another suggests 3.0% soap. It should be safe to assume that if surfactant levels used

to develop a wet-separation process are maintained well below those currently employed in the secondary recycling operations, no undesirable effects will occur to the finished paper product.

A system based on this principle could be employed directly by any sector producing high volumes of segregated paper such as institutions, office buildings, wholesalers, printers, and converters. These wastes are primarily mixed papers which can be hand sorted when market conditions are favorable for the supply of the high-grades. This system could also be used in conjunction with any of the other processes being developed to recover paper for recycling from mixed wastes. It has already been noted that the fibers extracted by these new waste sorters have found little use other than in the manufacture of construction paper or paper board because the grades are not separated. It is suggested that mixed papers produced from these separators could be further treated using low levels of surfactants to enhance recovery of the pulp substitutes from the inexpensive mix. If this could be achieved, higher uses for these papers would result which might justify the economics of the additional system.

Because of the promising results found by the author<sup>(31)</sup> and Liskowitz,<sup>(44)</sup> it was decided to develop a wet-paper separation process and investigate the wetting phenomena as it related to the controlled sinking of sized papers. A cross-section of paper samples was carefully selected with different properties to represent mixed papers which could originate from several office buildings or converter sources. With this diverse selection of papers it was possible to

isolate many parameters which controlled the wetting processes so that desirable recovery groups could be achieved. Besides having the ability to determine wetting rates on different sizing agents and additives, it was possible to make comparisons between bleached and unbleached papers, coated and uncoated papers, mechanically produced and chemically produced papers, and papers with different basis weights. While printed material is of interest to the deinking stage of wastepaper treatment, only unprinted papers were chosen for this study.

If a system could be developed to separate paper on a continuous basis, an economical alternative to the present methods could lead to increase the secondary fiber yields and reduce the recycling industry's dependency upon manual labor. A new separation technique would also help conserve our virgin-timber resources, reduce our solid-waste generation, save energy, and reduce pollution when recycled materials are substituted for virgin materials. It is anticipated that the wettability of various papers can be controlled by regulating the type and concentration of surfactant. Consequently, the variability of the wetting and sinking times of the various papers could be employed advantageously in a secondary fiber operation to recover similar papers for recycling.

To develop a paper separation process based on the wetting principles, it was necessary to acquire a representative sample of papers produced which could be found in the waste stream. The physical properties of the paper grades that were used throughout this work will be introduced first.

Because surfactants were used to accelerate wetting by lowering detention times, several had to be selected which had been proven to be excellent wetting agents in other paper or textile industrial applications. While the papers and surfactants have been used throughout this entire investigation, the work can be essentially divided into two parts. The first part is primarily concerned with the bench scale criteria to determine the parameters which govern the surface and capillary wetting processes. The laboratory studies include the determination of detention times and the size and shape effects during settling. Because the paper recycling method investigated in this study is based upon surfactant wetting, it is necessary to consider the wetting processes related to porous membranes. This involves a consideration of contact angles, surface tension, surface free energy, and the attractive forces between liquids and solids. Applications of these factors and their relationship to the wetting process are defined by adhesion,<sup>(45,46,47)</sup> cohesion, and spreading and liquid penetration into capillaries.

The fundamental wetting mechanisms were studied to explain the parameters which govern this separation process. After the thermodynamic principles have been presented, it will be appropriate to introduce the governing equations which directly apply to the wetting involved in this study. The phase of wetting where the liquid enters the pore spaces beneath the solid surface is important to a paper separation process using surfactant wetting. A general discussion of liquid penetration into a single capillary will be made before dealing

with the more complex problem of wetting the porous structure of paper.

Based on the laboratory findings using individual paper chips, a pilot plant process based upon surfactant preferential wetting was developed in the second phase of work.

## II THEORY

### WETTING OF POROUS MEMBRANES

All wetting processes are based upon the interaction of the wetting liquid and the nature of the substrate material. Because of the porous nature of paper, different wetting stages occur. Initially, surface wetting occurs as the liquid spreads over the solid. This is then followed by capillary wetting as the liquid penetrates the pores into the interior of the solid. Both of these processes to some extent overlap and take place simultaneously. Most of the important factors which are related to both steps include the surface tension, contact angle, capillary movement, spreading of the liquid over the solid, and the wetting power of different surfactants in contact with the sample.<sup>(48,49)</sup>

The nature of the paper surfaces is critical for the interaction with any wetting liquid. The chemicals used in the initial production phases, additives used to improve deficient paper properties, and bleaching methods all combine to produce different structures with surfaces having various chemical compositions, with many arrangements of functional or reactive groups all with different degrees of reactivity.

The equations developed in this section include the work of cohesion, adhesion, and spreading as well as those used to describe capillary penetration. These relationships are used to identify the effects of surface tension, contact angle, capillary movement, and surface spreading on the separation process.

#### ATTRACTIVE FORCES BETWEEN LIQUIDS AND SOLIDS

Because of the tendency to minimize the free energy of the system, a liquid drop will tend to form a sphere in the absence of gravity. In equilibrium, this shape exhibits the minimum area that the drop can occupy. If a drop is placed in contact with another substrate, either a solid or a liquid, an equilibrium state will occur where the free energy of the system is minimized. Gibbs<sup>(50)</sup> showed that for this to occur the following equation must be minimized:

$$\gamma_{LG}A_{LG} + \gamma_{SG}A_{SG} + \gamma_{SL}A_{SL} = \text{minimum}$$

where  $\gamma$  = surface energy, ergs/cm<sup>2</sup>

A = area

LG = liquid - vapor interface

SG = solid - vapor interface

SL = solid - liquid interface

Liquids experience unbalanced forces acting on the surface, by the material in the bulk of the fluid, which represent a form of energy of position. This is referred to as surface tension, or surface free energy,  $\gamma$ . Experiments have shown that these forces act within a range from less than a thousandth of a centimeter to perhaps less than one millionth. Physically, the surface tension of a liquid can



be viewed as the reversible work required to create a unit area of surface by stretching. The surface tension can be expressed as the force per unit length, usually dynes per centimeter, or as the potential energy per unit area, usually in ergs per centimeter squared. These units will be used throughout this work.

If an aqueous liquid is placed in contact with the surface of a paper, there are two situations which can occur. It might remain as a drop, resisting wetting, or it may tend to spread over and into the surfaces. As the liquid spreads over the surface it moves transversely while penetrating through the paper by capillary action where the liquid displaces the gas phase, which in this case is air containing vapor from the liquid. The most important factor which determines the extent to which wetting proceeds is the angle where the three phases meet. This is called the contact angle.

The contact angle is determined by the surface energy relationships of the solid and the liquid. Figure 2 shows the contact angle for a liquid and the paper solid for two cases. Diagram A shows the situation which exists when a poor wetting liquid is brought in contact with the paper sample. This situation is typical when water is used as the wetting agent on most all manufactured papers.<sup>(51)</sup> The large contact angle formed under this situation,  $\theta > 90^\circ$ , indicates extreme resistance to surface wetting and spreading with no interfacial penetration. Diagram B represents the situation which arises when a fair wetting liquid is brought in contact with the same surface.<sup>(52)</sup> The drop that forms produces a low contact angle,  $\theta < 90^\circ$ , which indi-

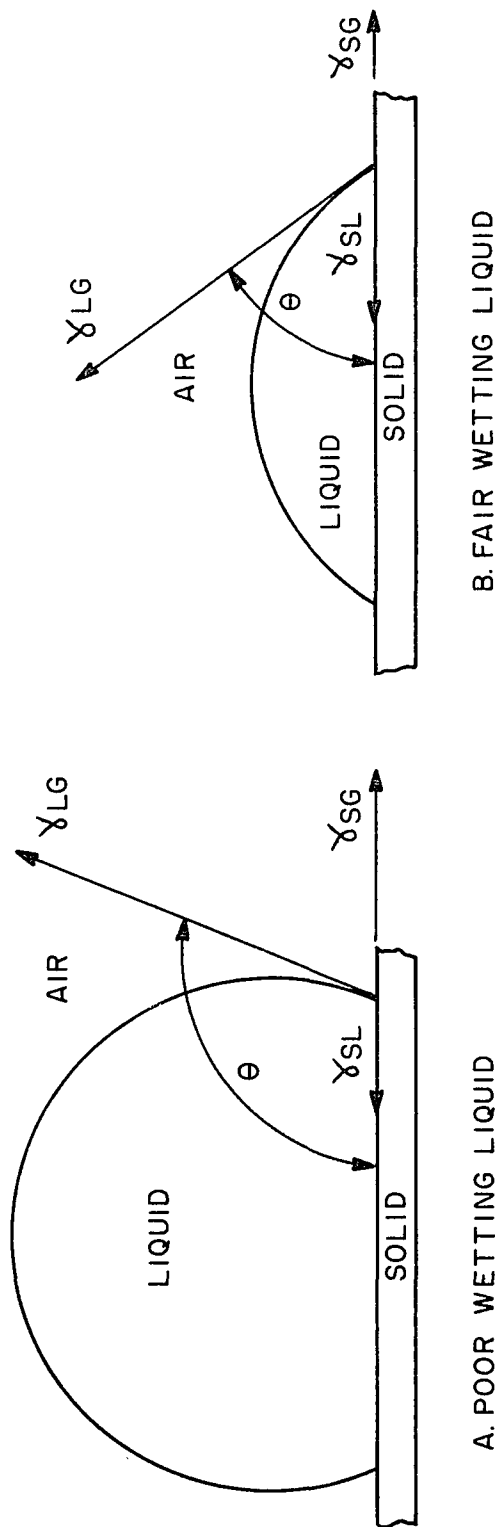


FIGURE 2. CONTACT ANGLES FORMED BY SOLID AND WETTING LIQUID

cates extensive wetting and spreading with an accompanying strong tendency to penetrate the porous structure. This situation occurs when liquids of low surface energy are applied to substances with high surface energies.

For the system shown in Figure 2, the minimization will be satisfied according to the following equation:

$$\gamma_{SG} - \gamma_{SL} = \gamma_{LG} \cdot \cos \theta$$

where  $\theta$  = contact angle.

This equation is a modified form from the one developed by Young.<sup>(53)</sup>

This equation assumes that the principal curvatures of the drop, which are mutually perpendicular to the normal planes, are constant. The free surface of the drop can therefore be viewed as a section of a sphere.

This equation can be rearranged to relate the contact angle directly to the surface energies:

$$\cos \theta = \frac{\gamma_{SG} - \gamma_{SL}}{\gamma_{LG}}$$

This equation clearly shows that the contact angle is a function of the affinity of the molecules of liquid to the molecules of solid (adhesive forces) to the affinity of the liquid molecules to themselves (cohesive forces).

An extreme situation where no interaction exists between the solid and the liquid would yield the following equation:

$$\gamma_{SG} = \gamma_{SL} - \gamma_{LG}$$

For this to occur the contact angle would have to be  $180^\circ$  which is

obviously impossible. This condition would represent the case where there were no adhesive forces between the solid and the liquid molecules only purely cohesive forces. There are appreciable attractions between all molecules and atoms.

For complete wetting to occur the contact angle would be reduced to  $\theta = 0^\circ$  to yield the following:

$$\gamma_{LG} = \gamma_{SG} - \gamma_{SL}$$

The condition where the contact angle is  $0^\circ$  has led to the definition of the spreading pressure:

$$\pi_{SG} = \gamma_S - \gamma_{SG}$$

where  $\pi_{SG}$  is the spreading pressure of a vapor on a solid,  $\gamma_S$  represents the surface energy of a solid against its own vapor, and  $\gamma_{SG}$  still refers to the energy of the solid in contact with the vapor of the liquid. When this is applied to the previous equation the following equation results:

$$\gamma_{LG} = \gamma_S - \pi_{SG} - \gamma_{SL}$$

This is known as Young's equation for zero contact angle.

#### WORK OF ADHESION, COHESION, AND SPREADING

Because of the attraction when a liquid is brought into contact with a solid, work must be done to separate them. This work is called the work of adhesion and is the direct measure of the free energy between the interaction of the liquid and the solid. This can be stated by the following expression:

$$W_A = \gamma_S + \gamma_{LG} - \gamma_{SL}$$

Where  $W_A$  is the work of adhesion. By combining the equation developed

from the spreading pressure, another equation forms:

$$W_A = \gamma_{SG} + \pi_{SG} + \gamma_{LG} - \gamma_{SL}$$

By introducing Young's equation, this equation can be rearranged to give

$$W_A = \gamma_{LG} (1 + \cos \theta) + \pi_{SG}$$

This expression for the work of adhesion, as a measure of the interfacial affinity, is known as the Young-Dupre equation. Bangham and Razouk reported that the vapor pressure is negligible for most finite values of  $\theta$ . Consequently, the  $\pi_{SG}$  term disappears so that the work of adhesion can be easily determined from the contact angle and the liquid surface tension.

If the solid substrate is not present, the work necessary to separate a unit area of a liquid from itself is called the work of cohesion. This situation would result in creating two new interfaces, so that, with  $\gamma_{SL} = 0$ , this work can be written as

$$W_C = 2\gamma_{LG}$$

where  $W_C$  = work of cohesion.

From these equations estimations can be made to determine the relative attractions between the solid and liquid molecules. For finite contact angles, cosine  $\theta$  will be less than unity so that  $W_A$  must be less than  $2\gamma_{LG}$  or  $W_C$ . Only when the contact angle  $\theta$  is zero, for a perfect wetting condition, can the situation be satisfied so that  $W_A$  is equal to or greater than  $W_C$ . For all finite  $\theta$ , the interattractive force between the solid and liquid is, in all cases, less than the cohesive force between the molecules in the liquid itself. At  $90^\circ$  the

adhesive force between the solid and liquid should be one half of the cohesive force of the liquid; and, at  $180^\circ$  the relationships could only be satisfied if there were no attractive forces between the solid and liquid. This extreme situation, as stated previously, obviously can not exist.

The differences between the work of adhesion and the work of cohesion can be used as a measure of the spreading between the liquid and solid. This work of spreading is therefore

$$W_S = \gamma_S + \gamma_{LG} - \gamma_{SL} - 2\gamma_{LG}$$

where  $W_S$  = work of spreading. Rearranging and substituting Young's equation yields the following expression when the spreading pressure is small:

$$W_S = \gamma_{LG} (\cos \theta - 1)$$

For all finite values of the contact angle, this expression yields negative values. Numerically this form of work increases with increasing values of both the surface tension of the liquid and the contact angle,  $\theta$ , between the solid and the liquid. Therefore spreading of a liquid on a solid is best accomplished using liquids of low surface tensions accompanied by low angles of contact.

#### PENETRATION OF A LIQUID INTO A CAPILLARY

Once the surface of a substrate has begun to wet, a liquid will proceed to penetrate through a porous material by capillary action.<sup>(54)</sup> This wetting stage depends upon the contact angle and the surface tension of the liquid. This process occurs in all directions where the material contains pores and cavities. To simplify the complex

structure of the fibrous cellulose which exists in paper, a single capillary tube will be discussed.

When a small capillary element is lowered into a liquid, the liquid will rise because of the adhesive forces between the liquid and the solid. A pressure difference exists across the interface which causes this spontaneous penetration. This relationship can be expressed by Laplace's law which is used to represent the meniscus of a liquid surface:

$$P = P_1 - P_2 = \gamma(1/R_1 + 1/R_2)$$

where  $P_1$  = pressure at the interface on the concave side of the meniscus,  $P_2$  = the pressure at the interface on the convex side of the meniscus,  $\gamma$  = the specific free energy of the liquid, and  $R_1$  and  $R_2$  = the radii of curvature of any two normal sections of the surface at right angles to each other.

It can be seen from this general equation that if  $P_1$  is larger than  $P_2$ , the interface will curve toward the gas phase, and that  $R_1$  and  $R_2$  will be positive or negative depending on whether the centers of curvature are situated inside the gas or the liquid phases, respectively.

If a uniform cylinder of constant radius  $r$  is used as the capillary element and the attractive forces cause a finite contact angle between the liquid and the solid phases of the capillary, the liquid surface becomes an element of a sphere so that  $R_1$  and  $R_2$  are equal. The resulting pressure difference can be expressed as follows:

$$P = \frac{2\gamma \cos \theta}{r}$$

This equation leads to some interesting implications. With an acute and finite contact angle, the pressure difference across the meniscus is positive and the liquid will spontaneously penetrate into the capillary. At large angles, where the cosine becomes small, the pressure becomes reduced. With contact angles greater than  $90^\circ$ , the cosine  $\theta$  becomes negative so that the pressure difference resists penetrating the capillaries. For capillaries in paper to best resist capillary wetting, this equation implies that the contact angle should be greater than  $90^\circ$  and the internal structure as closely compacted as possible to produce a small  $r$ .

The downward pressure caused by the gravitational forces acting on this capillary column of liquid of height  $h$  and density  $d$  is  $dgh$ . If this is equated to the previous expression, the resulting expression is developed:

$$h = \frac{2\gamma \cos \theta}{rdg}$$

This equation represents the maximum height that will occur in a vertical tube by capillary forces against gravitational forces.

Liquid penetration in a capillary system can be described using Poiseuille's equation for streamlined flow through a capillary. This general equation is expressed as follows:

$$\frac{dV}{dT} = \frac{\Delta P r^4 T \pi}{8\eta L}$$

where  $\frac{dV}{dT}$  = the volume rate of penetration of the liquid in the capillary,  $T$  = time of penetration,  $L$  = the distance penetrated in time



$T$ , and  $\eta$  = the viscosity of the liquid. Where  $P_e$  represents the sum of all the externally applied pressures, the hydrostatic head of the liquid and the pressure due to the capillary forces on the liquid-gas interface, this relationship can be integrated to yield

$$L^2 = \frac{rT}{4\eta} (P_e + \frac{2\gamma_L \cos \theta}{r})$$

where  $P_e$  = externally applied pressure difference plus the pressure due to hydrostatic head. When the previous expression for the pressure difference, where no external is applied and flow into a horizontal capillary takes place under capillary forces alone, is substituted into the above equation the following results:

$$L^2 = \frac{\gamma_{LG} r \cos \theta}{2\eta}$$

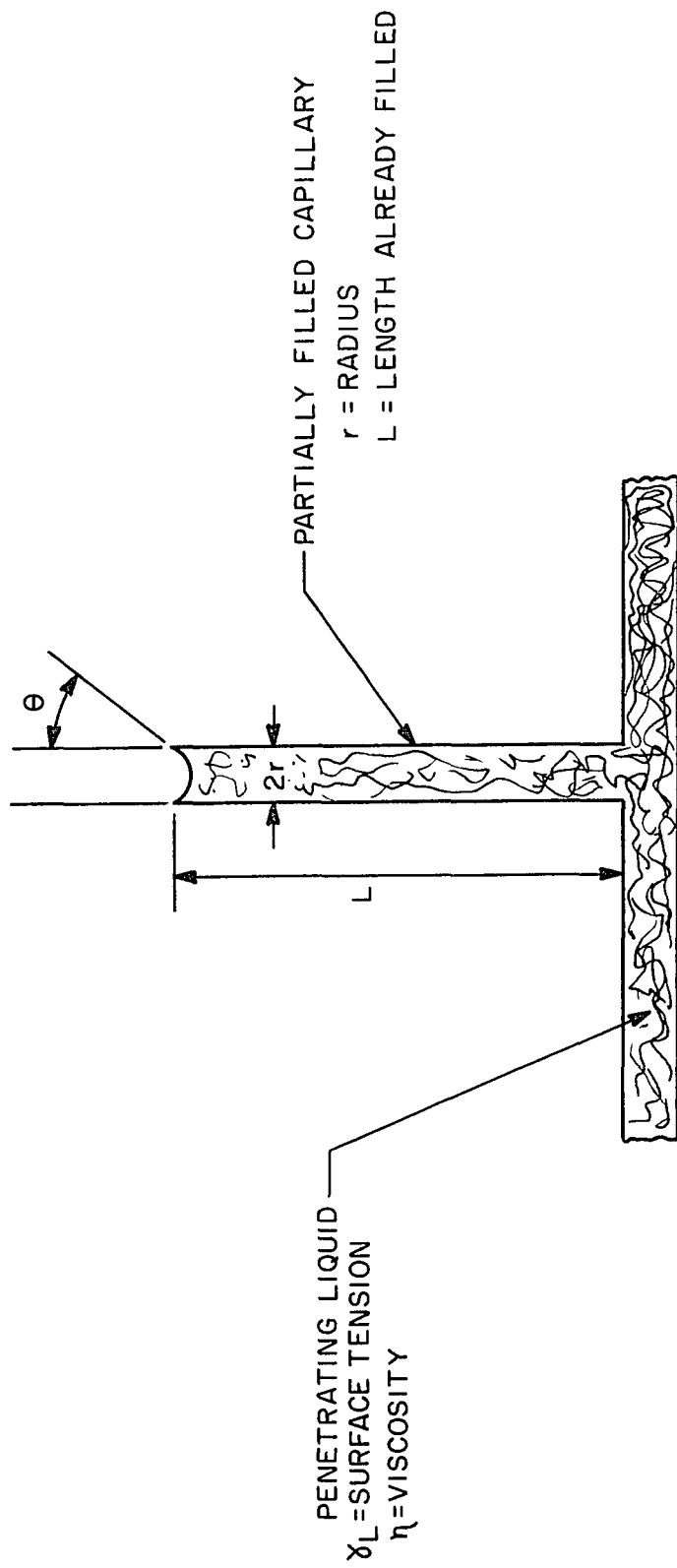
Differentiating this equation with respect to time yields the corresponding rate of penetration:

$$\frac{dL}{dT} = \frac{\gamma_{LG} r \cos \theta}{4\eta L}$$

This equation is generally known as the Lucas-Washburn equation<sup>(55)</sup> and is valid for laminar flow when the contact angle is acute, when gravitational and inertial effects are neglected, and when the viscosity of the displaced air is negligible.

Figure 3 represents the relationship for liquid flow through a single capillary tube. This is the form of capillary penetration that will be used to describe the paper wetting observed in this investigation. This situation has been observed by others interested in paper wetting.

$\theta$  = CONTACT ANGLE BETWEEN  
LIQUID AND CAPILLARY WALL



$$\text{TIME RATE OF PENETRATION} = \frac{dL}{dT} = \frac{r \gamma_L \cos \theta}{4 \eta L} \quad (\text{LUCAS - WASHBURN})$$

FIGURE 3. LIQUID FLOW THROUGH CAPILLARY TUBE

CAPILLARY PENETRATION OF A LIQUID INTO PAPER

The previous equations, while derived strictly for a single, uniform, cylindrical capillary, can be applied to the complex structure of porous paper. While the fibers are preponderantly orientated horizontally to the plane of the sheet, additional channels and cavities exist transversely, as well as perpendicular, to the axis of the sheet. The channels in paper resemble the pores within a bundle of cylinders. In this situation the liquid flows at one instant in a large pore which is next divided into streams before uniting with other streams at another large capillary. Although capillary penetration occurs in all these directions at different rates due to differences in the size, shape, distribution, and number of channels, an effective rate of flow can be described for flow in one direction. When this effective rate of flow is observed, an effective radius,  $r_e$ , is used to describe the geometry because of the tortuous nature of the actual channels.

Peek and McLean,<sup>(56)</sup> from studying the capillary rise of various liquids in porous materials, found that the theoretical rate of penetration did vary linearly with the reciprocal of height of rise. Furthermore, the dependency of the values for  $\gamma_L$  and  $\eta$  were identical to those established using fibrous paper as for a simple capillary. Because of the close agreement found between the theoretical expressions and experimental observations, the capillary wetting can be studied without knowing the size or size distribution of the capillaries present. By studying this wetting stage using various liquids on each separate porous material, the variations in the internal

structure can be eliminated.

For a certain system the factors such as densities, viscosities, size of capillaries, etc., can be considered constant so that the capillary wetting pressure can be determined by  $\gamma_{LG} \cdot \cos \theta$ . This term is present in all the capillary expressions used to represent the equilibrium value of the rise and also the rate of capillary penetration.

There are some similarities between this term and the expression developed for the surface spreading pressure, but there are also basic differences. At low contact angles both the surface and capillary wetting forms of wetting are improved. But, while surface spreading is enhanced by using liquids with low surface tensions, the reverse is true of the capillary wetting pressure. Numerically the capillary wetting pressure increases with increasing values of the surface tension of the liquid and decreasing values of the contact angle,  $\theta$ , between the solid and the liquid. The surface tension affects the wetting processes differently being dependent upon the physical structure and the chemical composition of the solid, i.e. the degree to which the pores are present in the solid for the liquid to penetrate and the chemical activity of the sites in the material. The wetting process of any solid may be quite different depending upon the strength of the surface spreading pressure or the capillary penetration pressure.

### III EXPERIMENTAL MATERIALS AND PROCEDURES

#### SELECTION OF PAPER GRADES

The papers that were used in this study were carefully selected to represent the bulk of papers produced in this country and, also, those which could be encountered in the solid waste streams of many commercial or institutional facilities. These samples intentionally did not include the broad spectrum of paper containing laminates, sanitary tissue, polymer coatings, or construction products. The paper stocks were supplied by the Technical Center of the St. Regis Paper Company, West Nyack, New York. They included bleached and unbleached papers consisting of groundwoods, fine and coarse papers, and a special food board. These papers are described in Table 7 with an abbreviated description used in some of the other tables.

#### Groundwoods

Three bleached papers were selected to study the recovery behaviors of the important groundwood group which includes newsprint, commercial printing papers, and offset book papers. Two of these samples were uncoated. One was an offset book printing paper which was surface sized with enzyme converted corn starch. Another was a catalog, or directory paper, internally sized with rosin. A clay coated

| <u>DESCRIPTION</u> | <u>PAPER TYPE</u>             | <u>PAPER COMPOSITION</u>                     |
|--------------------|-------------------------------|--|
|                    |                               | <u>BLEACHED</u>                              |
| Printing           | 45-1b offset printing         | Groundwood, uncoated, starch surface size    |
| Catalog            | 30-1b lettergrade catalog     | Groundwood, uncoated, rosin internal size    |
| Textweb            | 38-1b coated textweb          | Groundwood, clay coated, rosin internal size |
| Regular-strength   | 50-1b multiwall shipping sack | Kraft, uncoated, regular strength            |
| Wet-strength       | 50-1b multiwall shipping sack | Kraft, uncoated, wet strength                |
| Foodboard          | 105-1b cup sidewall           | Sulphite, wax coated, sized                  |
| Bond               | 75 g/m <sup>2</sup> bond      | Sulphite, uncoated, sized                    |
|                    |                               | <u>UNBLEACHED</u>                            |
| 40-1b              | 40-1b shipping sack           | Kraft, uncoated, regular strength            |
| 50-1b              | 50-1b shipping sack           | Kraft, uncoated, wet strength                |
| 60-1b              | 60-1b shipping sack           | Kraft, uncoated, regular strength            |

TABLE 7. PAPER GRADES USED IN RECOVERY SYSTEMS

textweb which could be found in magazines, booklets, or brochures was included. This was also internally sized with rosin.

#### Coarse Papers

Two bleached and three unbleached kraft shipping sacks, similar to grocery bags, were used to represent coarse papers which account for 20 to 25 percent of the total annual paper production. The bleached samples were multiwall shipping sacks, uncoated, and internally sized with rosin. One had been produced with a wet-strength additive, while its counterpart did not have this application. They both had the same basis weights. Similarly, the unbleached samples were shipping sacks, uncoated, and sized with rosin. They, however, had different weights of 40, 50, and 60 pounds. In addition, one of them was a wet-strength paper, while both of the others were regular-strength.

#### Special Food Board

A thick, heavy cup sidewall sample was selected to represent the food boards such as frozen food or milk cartons, or ice cream containers. This cup-type container was a bleached sulphite which had been heavily coated.

#### Fine Paper

A bleached sulphite bond paper was chosen from the wide range of fine paper products. This group comprises approximately 13 percent of the total annual paper production and includes drawing papers, bristols, and checks.

Because the papers used throughout this study were selected to represent a broad range of those which could be found in a selected solid waste stream, it was desirable to determine some of their physical properties and to list an estimate as to their raw fiber derivation and in the manufacturing process used in pulping. The results are shown in Table 8.

The basis weights are calculated as the weight of substance per unit area where the areas are measured in reams. The groundwood reams are measured in 3,300 square feet; the non-groundwood reams, in 3,000 square feet.<sup>(57)</sup> The next column where all basis weights have been converted to S I units, can be used to make comparisons between the different grades. The unit weights vary from  $44.4 \text{ g/m}^2$  for the catalog paper to  $170.9 \text{ g/m}^2$  for the heavy cup foodboard.

The sheet thicknesses were determined with a caliper on single sheets taking the average of several readings. The thicknesses vary from 0.076 mm for lightest sample to 0.286 mm for the heaviest one. The apparent densities can be calculated from the basis weights and thicknesses. Because the paper thickness at a constant basis weight can vary over wide limits, the densities can similarly vary. Density values can be as low as  $0.1 \text{ g/cm}^3$  for creped wadding paper or as high as  $1.4 \text{ g/cm}^3$  for glassine. The values for these papers vary from  $0.43 \text{ g/cm}^3$  for an unbleached paper to  $0.66 \text{ g/cm}^3$  for the bond sample within a narrow band.

The next four columns estimate the pulp composition for the finished paper samples. The composition was divided into groundwood,



| ESTIMATED PULP COMPOSITION |                          |                                   |                        |                                   |                    |                          |                        |                        |                            |
|----------------------------|--------------------------|-----------------------------------|------------------------|-----------------------------------|--------------------|--------------------------|------------------------|------------------------|----------------------------|
| Paper Sample               | Basis Weight             | SI Un.Wt.,<br>(g/m <sup>2</sup> ) | Av.Sht. Tkns.,<br>(mm) | App. Den.<br>(g/cm <sup>3</sup> ) | Groundwood,<br>(%) | Softwood Sulfite,<br>(%) | Softwood Kraft,<br>(%) | Hardwood Kraft,<br>(%) | Fiber Lg. Wtd.Av.,<br>(mm) |
| Printing                   | 45#/3300ft <sup>2</sup>  | 66.6                              | .127                   | .52                               | 70                 | -                        | 15                     | 15                     | 1.0                        |
| Catalog                    | 30#/3300ft <sup>2</sup>  | 44.4                              | .076                   | .58                               | 70                 | -                        | 30                     | -                      | 2.4                        |
| Textweb                    | 38#/3300ft <sup>2</sup>  | 56.2                              | .095                   | .59                               | 60                 | -                        | 40                     | -                      | 1.7                        |
| Reg-Str.                   | 50#/3000ft <sup>2</sup>  | 81.4                              | .152                   | .53                               | -                  | -                        | 50                     | 50                     | 2.4                        |
| Wet-Str.                   | 50#/3000ft <sup>2</sup>  | 81.4                              | .152                   | .53                               | -                  | -                        | 50                     | 50                     | 2.4                        |
| Foodboard                  | 105#/3000ft <sup>2</sup> | 170.0                             | .286                   | .60                               | -                  | 50                       | -                      | 50                     | 2.4                        |
| 40-1b                      | 40#/3000ft <sup>2</sup>  | 65.1                              | .114                   | .57                               | -                  | -                        | 90                     | 10                     | 3.3                        |
| 50-1b                      | 50#/3000ft <sup>2</sup>  | 81.4                              | .190                   | .43                               | -                  | -                        | 90                     | 10                     | 3.3                        |
| 60-1b                      | 60#/3000ft <sup>2</sup>  | 97.6                              | .178                   | .55                               | -                  | -                        | 90                     | 10                     | 3.3                        |
| Bond                       | 46#/3000ft <sup>2</sup>  | 75.0                              | .114                   | .66                               | -                  | 60                       | 20                     | 20                     | 3.1                        |

TABLE 8. PAPER GRADE PROPERTIES

softwood sulfite, softwood kraft, and hardwood kraft groups. The last column lists the fiber lengths for the individual papers. These fiber dimensions are the weighted averages based upon results from the College of Forestry, State University of New York, as reported by Casey. (58)

### SELECTION OF SURFACE-ACTIVE AGENTS

The surfactants selected to preferentially wet and separate the papers included several nonionics and ionics. Table 9 summarizes the basic features for each of the surfactants by charge group. This table includes for each of these groups the commercial name, the manufacturer, an abbreviated class description, and formula.

#### Cationic Surfactants

The relatively long-chain cationics chosen can be exemplified by the common quaternary ammonium salt,  $RN(CH_3)_3Cl$ , where R is a hydrocarbon radical having hydrophobic characteristics which is positively charged.

#### Anionic Surfactants

The table shows that as a group the anionic surfactants are generally made up of hydrophobic radicals of fatty acid hydrocarbon chains,  $CH_3(CH_2)_nCHOSO_3$ , fatty alcohol sulphates, or as mixtures of aliphatic and aromatic hydrocarbons,  $CH_3(CH_2)_nC_6H_4SO_3$ , alkyl aryl sulphonate. While the hydrophobic end is positively charged, the sulfo group,  $-SO_3$ , accounts for their anionic hydrophobic behavior.

#### Non-ionic Surfactants

The non-ionic surfactants selected are effective in both acid and alkaline media. The hydrophilic part of all these molecules is

| <u>TRADE NAME</u> | <u>MANUFACTURER</u> | <u>CLASS</u>   | <u>FORMULA</u>  |
|-------------------|---------------------|--|---|
| <u>CATIONIC</u>   |                     |  |   |
| Amine T           | Ciba-Geigy          | Heterocyclic Tertiary Amine  | $C_{18}H_{37}NC_2H_4NC_2H_4OH$                          |
| CPC               | Fine Organic        | Cetyl Pyridinium Chloride  | $C_5H_5N(CH_2)_{15}CH_3Cl$                              |
| G-3634A           | ICI America         | Quaternary Ammonium Derivative                                     | $RN(CH_3)_3Cl$  |
| G-2090            | ICI America         | Polyoxyethylene Fatty Amine and<br>Polyoxyethylene Sorbitol Oleate | $C_{66}H_{128}O_6(OH)_4$<br>$C_{60}H_{121}O_{21}NH_2OH$ |
| <u>ANIONIC</u>    |                     |  |   |
| Calsolene Oil     | ICI America         | Sulfated Fatty Acid Ester  | $RCO_2SO_3Na$   |
| G-3300            | ICI America         | Alkyl Aryl Sulfonate (ABS)   | $[CH_3(CH_2)_{10}]_2CHC_6H_5SO_3Na$                     |
| Neutronyx S60     | Onyx Chemical       | Ammonium Salt of Sulfated<br>Alkylphenol Polyglycol Ether          | $C_4H_7C_6H_4OC_{12}O_6SO_4NH_3$                        |
| Maprofix 60S      | Onyx Chemical       | Sodium Lauryl Ether Sulfate  | $C_{12}H_{25}OSO_4Na$                                   |
| <u>NONIONIC</u>   |                     |  |   |
| Renex 30          | ICI America         | Polyoxyethylene Tridecyl Ether                                     | $C_{39}H_{77}O_{14}OH$                                  |
| Tween 20          | ICI America         | Polyoxyethylene Sorbitan Monolaurate                               | $C_{60}H_{118}O_6(OH)_4$                                |
| G-2109            | ICI America         | Polyoxyethylene Coconut Fatty Acid                                 | $C_{38}H_{77}O_{13}OHCOOH$                              |

TABLE 9. SURFACE-ACTIVE AGENTS USED IN RECOVERY SYSTEMS

typical of most surfactants that are found in this group. It consists of polyoxyethylene as a chain of  $-(CH_2-CH_2-O)-$  groups bound to the hydroxyl (OH) hydrophilic functional group.

#### LABORATORY BENCH SCALE PROCEDURES

##### Detention Times

Wetting tests were conducted to determine the wetting and ultimate sinking times of all the paper samples with water and various concentrations of different surfactants. This was done to find if desirable separations could be obtained from the paper mixture so that this approach could be employed advantageously in a secondary fiber operation to recover similar papers.

For the majority of these tests, ten paper chips from each of the ten paper samples were added to vessels containing various concentrations of surfactants. The paper chips were scissor-cut to approximately one square inch. Fifty gallon fish tanks with surface areas of 4.5 square feet were used to contain the liquid and the paper chips.

Initially, the surfactants were diluted with deionized water to make various concentrations ranging from 0.005 to 1.00 percent. After the tanks were filled to a liquid depth of approximately two inches, the liquids were vigorously agitated by hand to insure uniform mixing and reduce excessive foaming. In a few minutes excess foaming ceased and the paper chips were initially resting on the liquid surface, not on a soap bubble. Both sides became wetted during this operation.

Observations were made at regular intervals to determine the

number of chips for each paper sample that remained floating or had already sunk. Each of the chips had been lightly marked with a pencil so that the paper grades could be identified when removed from the bottom of the tank. A record for the floating and sinking papers was made initially, at time periods of 10, 20, 30, and 45 minutes, then, every 15 minutes till two hours had elapsed, and subsequently, at half-hour periods until a total of ten hours had transpired from the initial paper immersion. Further observations were made at irregular intervals when required. At each observation period the papers that had sunk to the bottom of the tank were removed and the floating papers were gently agitated to dislodge any chips that were overlapping and touching and to assure that each chip had full access to the liquid surface to accelerate its individual wetting and sinking.

The tanks were washed several times with deionized water between tests to remove any traces of the previous surfactant.

#### Surface Tensions

In order to determine the surface tension values for the different wetting liquids, the duNoüy ring method was used according to the procedure outlined by the ASTM Committee D-12 on soaps and other detergents. This technique is given the ASTM designation D1331-56 (re-approved 1970) and is titled "Standard Methods of Test for Surface and Interfacial Tension of Solutions of Surface-Active Agents."<sup>(59)</sup>

All measurements were made using a 4.00 cm mean circumference platinum, with a 40.0 R/r value, and the duNoüy precision tensiometer

placed level on a well supported table free from vibrations and other disturbances. The glassware was thoroughly cleaned in acid before being rinsed in distilled water. The platinum ring was cleaned, rinsed, and then heated over a gas flame before all measurements. The torsion balance was calibrated according to the ASTM procedure in order to determine the conversion factor and scale readings.

Although a number of different methods can be used to measure the surface tension such as using Lord Rayleigh's equation, Sentis' measurements using drop volumes, Jaeger's procedure based on the maximum bubble pressure, and Quincke's drop-weight method based on dimensional analysis,<sup>(60)</sup> the duNoüy ring procedure was used in this investigation because of the availability of the equipment.<sup>(61)</sup>

Various liquids were used to verify the calibration of the tensiometer. These included distilled water, methanol, ethanol, benzene, glycerol, and hexane. Their surface tensions determined in dynes per centimeter were compared with standard values tabulated and published in the Handbook of Chemistry and Physics. The surface tensions were then determined, using two measurements for each concentration of 0.01, 0.1, 1.0, and 5.0 percent, for a cationic quaternary ammonium derivative surfactant and an anionic alkyl aryl sulfonate detergent. The temperature was maintained at 72°F throughout the measurements.

### Contact Angles

The contact angles determined in this study were directly measured using a contact angle goniometer which is capable of resolving the image of sessile drops on the surface of the paper samples. Fig-

ures 4 and 5 shows the Ramé-Hart, Mountain Lakes, N.J., Model A-100 goniometer used to accurately determine these angles. The instrument was originally developed by the Surface Chemistry Branch of the Naval Research Laboratories under the direction of W.A. Zisman.<sup>(62)</sup>

The contact angle goniometer consists of a channeled horizontal optical bench equipped with leveling screws on which three independent assemblies are mounted: 1. The optical system, consisting of a horizontal low-power microscope assembly, is equipped with rack and pinion focusing, and a built in direct-reading goniometer scale with two independently mounted crosshairs. 2. The specimen stage possesses provisions for controlling the motion in both the vertical and the lateral direction transverse to the optical axis. The stage is equipped with a ball and socket joint and four jack screws to permit tilting and leveling of the specimen. 3. The illuminating system is equipped with a variable intensity control box, color filters, and an iris diaphragm.

The optical system provides an overall magnification of 15.4 X and a mechanical working distance, from the objective to the specimen, of 65 mm. To allow for direct reading of the contact angle, the goniometer head is equipped with two independently rotatable crosshairs, each mounted as a diameter of the telescope. When one crosshair is set parallel to the base of the stage, the other can be rotated, using a 360° -scale in a plane at right angles to the microscope axis, so that the scale can be adjusted to read the contact angles. As this crosshair rotates, a pointer which is attached and parallel also rotates about the microscope. The angular displacement could then be

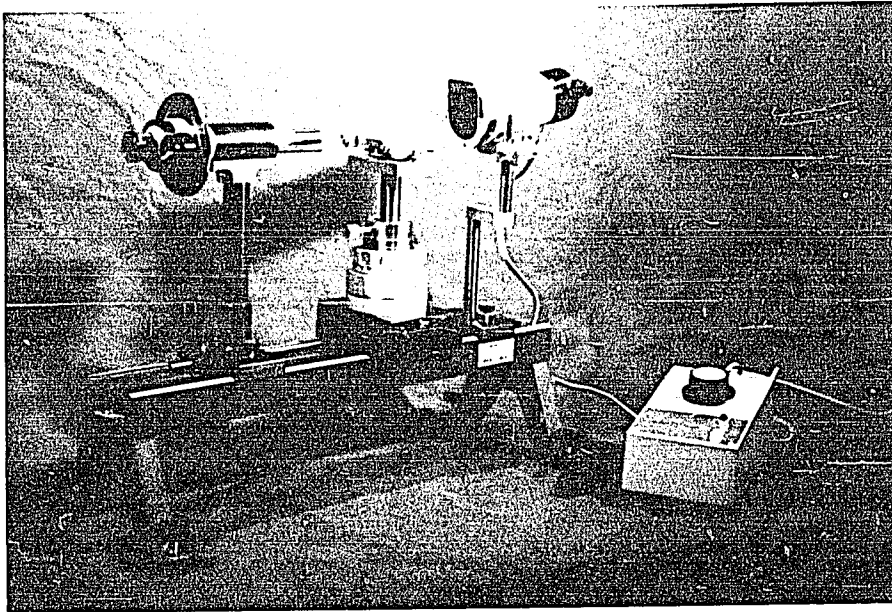


FIGURE 4. RAMÉ-HART MODEL A-100 GONIOMETER USED TO DETERMINE CONTACT ANGLES

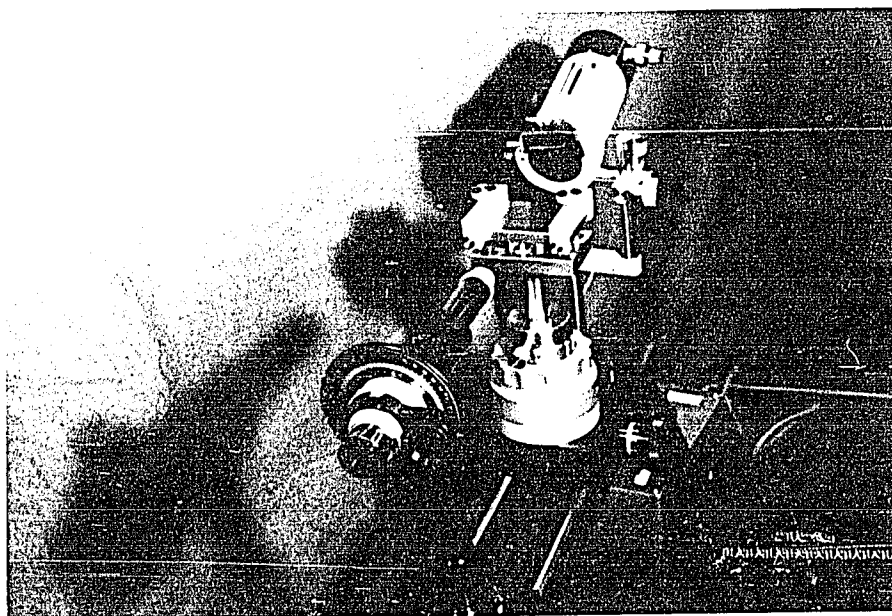


FIGURE 5. TOP-VIEW OF GONIOMETER SHOWING EYE-PIECE, STAGE, AND ILLUMINATOR



read directly from the scale using a magnifier. Fine focusing of the image was accomplished with a rack and pinion mechanism connecting the stage and the microscope on top of the bench. To increase the accuracy of the goniometer scale readout, a magnifier was used to permit the estimation of the contact angle to 0.5 degrees.

The specimen stage has a rectangularly shaped stainless steel surface mounted on a movable supporting column. The vertical and transverse horizontal motions are calibrated in 0.02 mm divisions so that the goniometer can be used to measure the liquid droplets. The stage features a ball and socket joint with four screw jacks so that tilting or leveling of the specimen can be achieved.

The paper substrates that were studied were cut in the form of strips, 2 to 3 mm thick, and placed on the specimen stage. A pair of stainless steel clamps, secured directly to the stage, were used to eliminate rippling of the specimen by exerting a slight tension on the films.

A 2-ml hypodermic syringe was used to place a drop of the liquids studied on the solid. This syringe was equipped with a No. 23 stainless steel needle which could give 50 to 100 drops per ml.

The tip of the hypodermic needle was manually held between 2 to 5 mm from the surface of the strip as each drop was deposited on the paper. Approximately five seconds were required after placing the drop, to focus and align the microscope and set the goniometer cross-hairs for the first contact angle reading. Subsequent readings were

made through continuous observation and recorded at appropriate time intervals using an electric timer which read in seconds.

Two photographs are included to show how the contact angles can be determined. Figures 6 and 7 are enlargements of a droplet and a solid image for fairly high contact angles as seen by an observer through the eyepiece. The angles are measured by fine adjustments with the crosshairs.

The contact angle measurements were conducted at an average temperature of 72°F and a relative humidity of 70 percent. The measurements were made on all the paper samples using deionized water and various concentrations of surface-active agents diluted with deionized water.

The contact angles were measured and recorded at various time periods so that their transient behavior could be determined and compared with other samples. As previously mentioned, the first observation required approximately five seconds of elapsed time from the initial placement of the droplet to the first reading. Although continuous monitoring of the drop was performed, readings were subsequently made at the 30 sec, 45 sec, 60 sec, and additional 30 sec time periods through 14 minutes or until the drop disappeared.

The contact angles were measured on one side of the drop at the interface a minimum of four times, twice on each side of the paper sample, to determine if appreciable differences existed between the screen and felt sides or coated sides and, also, to establish consis-

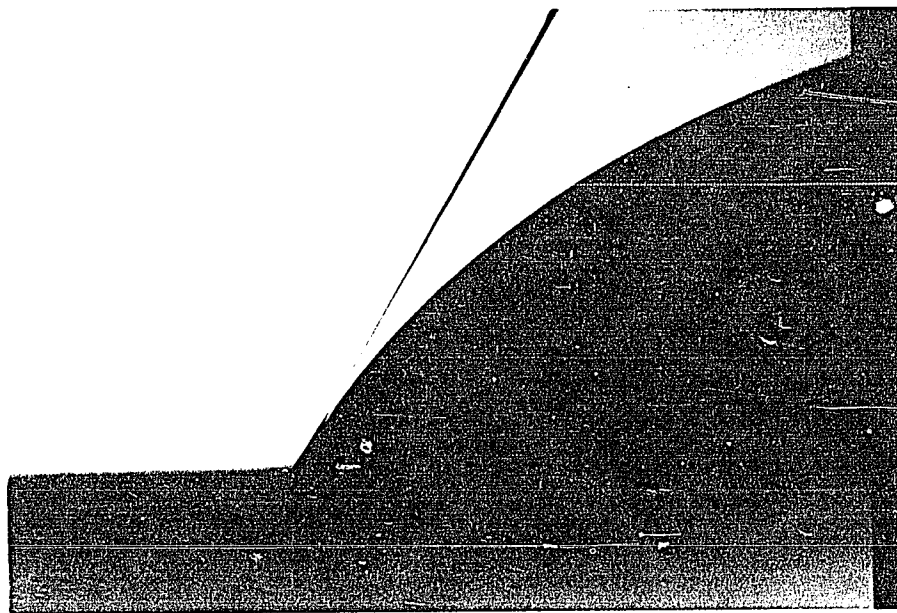


FIGURE 6. ENLARGEMENT OF LIQUID-SOLID INTERFACE FOR 61° CONTACT ANGLE

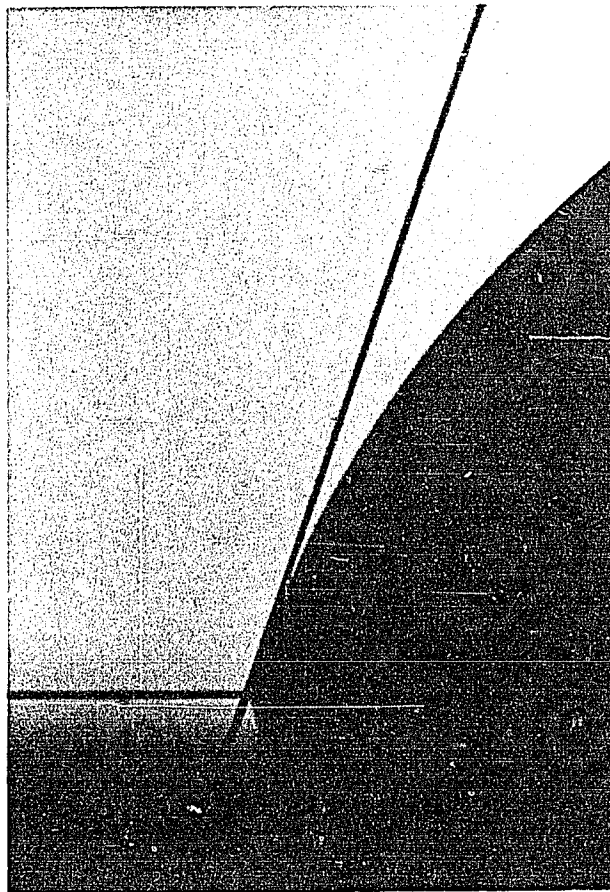


FIGURE 7. ENLARGEMENT OF LIQUID-SOLID INTERFACE FOR  
72° CONTACT ANGLE

tent surface wetting behaviors. Although some slight variations existed due to the procedure and paper irregularities, it was found that these could be minimized through practice. When appreciably different wetting characteristics were observed due to the paper production, either the paper formation or the chemical additive process, the wetting on the most resistant side was selected to represent that sample.

The most popular methods used for direct contact angle measurements involve a sessile drop placed on the solid under investigation.<sup>(63)</sup> The contact angle can be determined by projecting an enlarged image on a screen and measuring there, photographing the drop profile, or directly using a goniometer mount on a telescope.<sup>(64,65)</sup> For contact angles less than  $90^\circ$ , another procedure measures the angle at which light from a source is reflected from the contact point of the drop and solid. For viscous fluids Derjaguin<sup>(60)</sup> investigated a procedure using either a vertical rod or plate which was partially immersed in a liquid so that the angle could be directly measured. Another method employs a tilting plate in a horizontal liquid surface where direct measurements of the slope of the solid surface at the boundary line can be observed.<sup>(60)</sup>

The contact angle can be computed indirectly by measuring the thickness and height of a sessile drop on a plate using geometric relationships developed by Bikerman, Bashforth, Adams, or Poisson.<sup>(60)</sup> Other geometric relationships exist between the drop volume and base diameter. Capillary rise tests can be conducted so that the contact

angle can be calculated from the basic equations governing that process or by measuring pressure differences required to cause capillary movement for various liquids. Tensiometric methods can also be used which measure the force exerted on a thin plate or ring when it is wetted by a liquid. Ablett's method<sup>(60)</sup> employs a cylinder which is partially immersed in a liquid so that geometric relationships can be applied. A modification of this method substitutes a sphere for the cylinder. Because of the ease of operation, the reproducibility of the results, and success in other paper applications, the sessile drop method was used in this study.

#### Capillary Penetration

Because of the difficulties encountered in determining the equilibrium value of the height of capillary penetration,<sup>(67,68,69,70,71,72)</sup> it was decided to study the rate of capillary rise to measure the second wetting process. The rate of capillary rise was measured in strips of paper using the apparatus, see Figure 8, constructed for this purpose. The apparatus was built as a humidor inside which the strips of all the paper samples were placed vertically into large plastic troughs partially filled with the wetting liquids to be tested.

In studying the liquid penetration into the samples, strips about 2.0 cm wide and about 15.0 cm long were used. They were lightly marked with a pen every half-centimeter along the length to facilitate reading the liquid movement. The tops of the paper strips were clamped to a wooden holder so that the lower end could be dipped in-

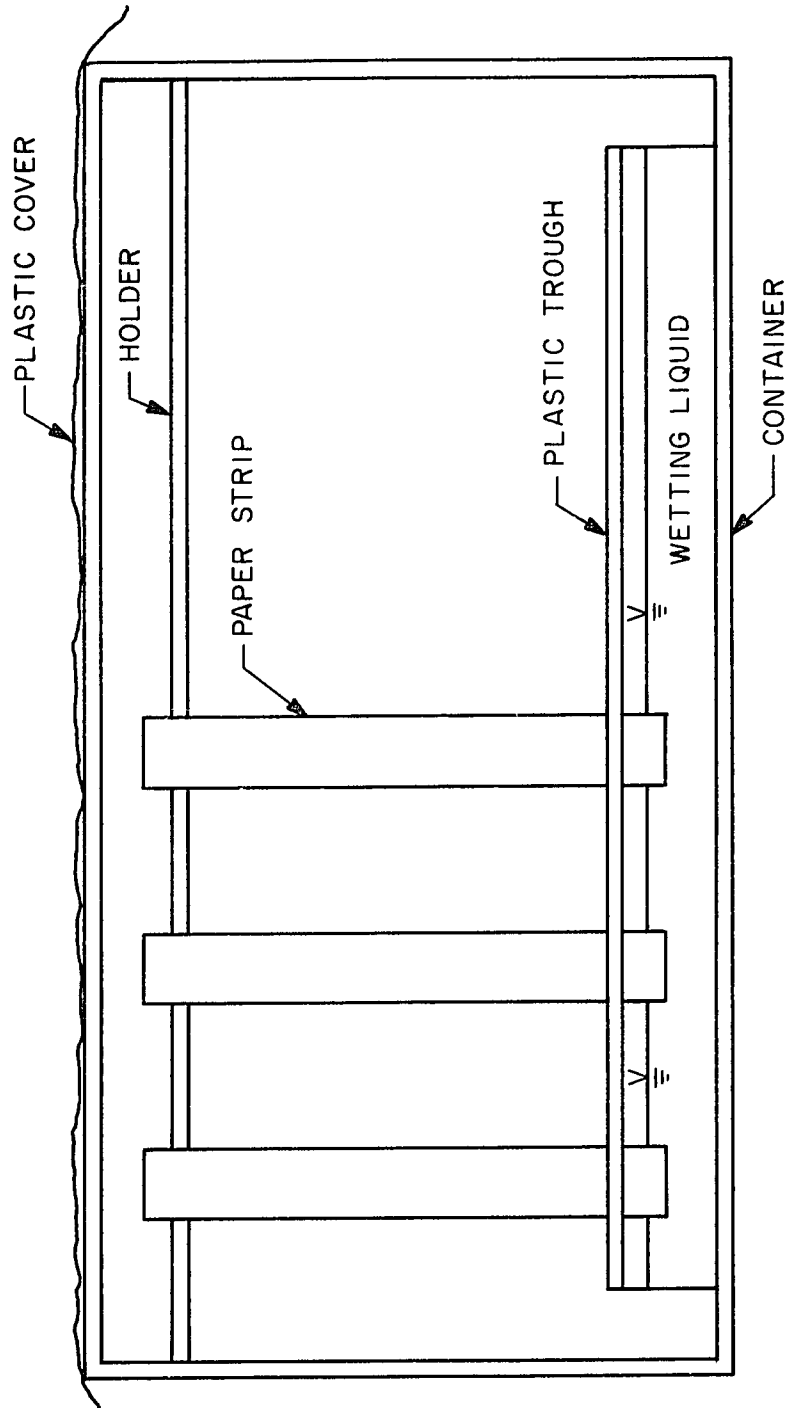


FIGURE 8. APPARATUS FOR MEASURING CAPILLARY RISE IN PAPER STRIPS

to the liquid. Before capillary rise measurements were conducted, the strips were attached to the holder and the troughs were placed under the strips carefully to avoid contact with them. Water was then added on the floor of the container, the tank was covered with a plastic cover, and the strips were then allowed to reach equilibrium with the temperature and humidity inside the chamber.

After water vapor had condensed on all visible surfaces of the contained, a corner of the plastic cover was lifted so that the wetting liquids could be added to the troughs avoiding splashes. After an initial reading, subsequent rise measurements were recorded at times of 5, 10, and 15 minutes, then at 15 minute intervals until 1.5 hours of total elapsed time, and finally every 30 minutes until capillary rise ceased or exceeded the strip length. When the liquid rose in the strips, the upper portion of the wetted region was always clearly demarcated from the unwetted area. Capillary fall tests were also performed on some of the wetting liquids by modifying the apparatus. The procedures followed were almost identical.

#### Paper Shape and Size Effects

Paper samples were cut into various sizes and shapes to determine these effects on the wetting and sinking processes. To measure the shape and size effects, tanks were nearly filled with different surfactant concentrations to which the various paper chips were introduced.

Paper samples were cut into regular and irregular shapes of different sizes. The regular shapes included squares with dimensions of



0.5, 1.0, 1.5, and 3.0 inch sides, and circles with 1.0, 2.0, and 3.0 inch diameters. The irregular shapes had smooth edges which varied from 0.5 to 3.0 inches in size. Figure 9 illustrates the various sizes and shapes for a bleached paper grade used in these determinations.

As performed and described previously, for the one-inch square chips, the various papers were scattered over the liquid surface. The chips were then gently agitated to insure wetting on both sides initially. The chips were then allowed to float on the liquid where the initial wetting process took place. Observations were made on a regular basis to determine the number of paper chips that were still floating and those that had wetted and sunk. Figure 10 shows the tank with the various sizes and shapes floating on the surfactant liquid. This picture illustrates appreciable touching and overlapping of the various chips on the liquid surface. The bottom of the tank shows several chips that have already wetted and sunk.

In order to determine the quiescent settling characteristics of discrete papers during sinking, a clear plexiglass column was constructed. Figure 11 shows a picture of this column which is six feet long with a ten inch inside diameter. A measuring tape was attached to the outside of the column.

Various surfactant concentrations, which had been pre-mixed, were poured into the tube and given time for the excess foam to dissipate. It took approximately ten minutes for the foaming to cease and the liquid to reach an equilibrium state.

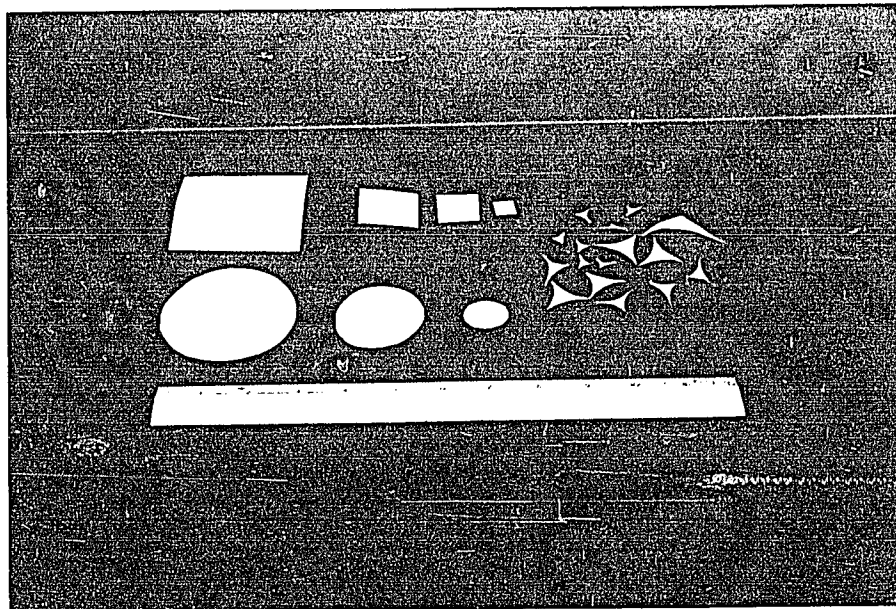


FIGURE 9. VARIOUS CHIPS OF BLEACHED PAPER GRADES USED TO DETERMINE SIZE AND SHAPE EFFECTS ON RECOVERY SYSTEMS

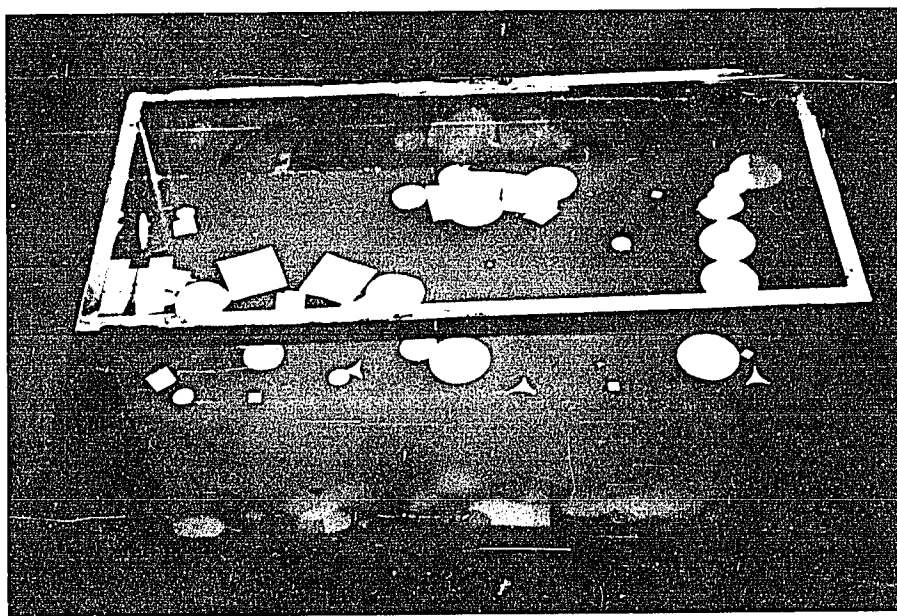


FIGURE 10. SETTLING TANK FILLED WITH SURFACTANT SHOWING PAPER CHIPS FLOATING ON SURFACE

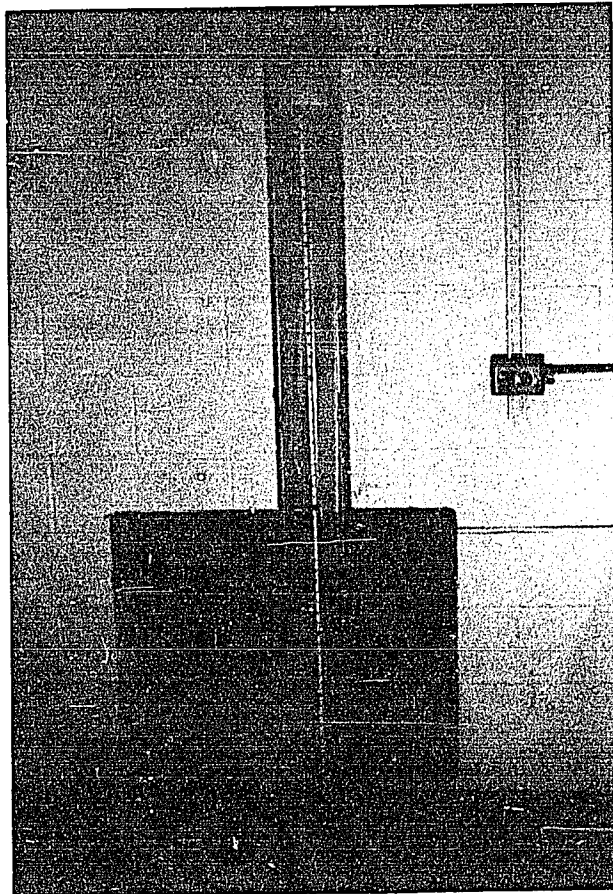


FIGURE II. PLEXIGLASS COLUMN FILLED WITH SURFACTANT  
USED TO DETERMINE SHAPE EFFECTS ON SETTLING  
RATES

As done for other wetting and sinking measurements, square and circular paper chips were initially wetted on both sides when introduced to the wetting liquid. The chips floated on the surface where the initial wetting process took place. Once the chips started to settle, an electric timer was used to record the elapsed time required for the chips to fall every six inches, until they reached the bottom. The sizes of the circular chips were 1.0, 2.0, and 3.0 inches in diameter; the squares were 1.0, 1.5, and 3.0 inches on a side.

#### CONTINUOUSLY MIXED PILOT PLANT

##### Physical Features of Demonstration System

A plexiglass tank, 2 feet by 4 feet by 3 feet high, was used throughout this part of the study. The clear sides allowed for visual observations to study the wetting, mixing, and sinking processes. This tank had a large surface area and volume so that loading rates could be determined on either basis.

A Lightnin' mixer was used to agitate the papers after they were introduced into the liquid. The motor had a 5 amp rating and was equipped with a variable speed control. The speed of the propeller could be adjusted from zero to 1750 rpm. An ampmeter was used to measure the power input at various mixing speeds and, also, serve to protect the motor.

In order to induce mixing to the papers after they had been added to the tank, various propeller sizes and arrangements, including

conventional general purpose and special purpose models, were studied. All of these proved to be unacceptable. It was found that, in order to provide sufficient agitation to circulate the papers, the mixer was required to operate at extremely high speeds between 1500 and 1800 rpms. At these violent speeds it was found that all paper samples were sucked below the liquid surface and the individual chips were promptly shredded by the propellers. These shredded fibers sank almost immediately regardless of the wetting agent and concentration so that no separations could be achieved. A washing machine agitator was found to provide satisfactory mixing without any shredding problems with mixing speeds up to 100 rpms. The one used measured 12 inches at its base, 15 inches high, and had three spiral vanes. A picture of this propeller used in all recovery determinations is shown as Figure 12. A stainless steel shaft was used to connect the propeller to the motor.

The papers used in the recovery system included all five kraft shipping sacks. The bleached papers were the 50-lb samples; the unbleached papers were the variously weighted samples.

Paper chips for each of these samples were made with a hand operated paper cutter. These chips varied between rectangles and squares with all combinations of dimensions from  $1/8$  to three inches on a side. Figure 13 shows a photo close-up of the chips used for an unbleached sample. It clearly shows narrow rectangles as well as larger ones. The most common sizes produced were squares with  $1\frac{1}{2}$  inch sides. These sizes and shapes were typical for the other four

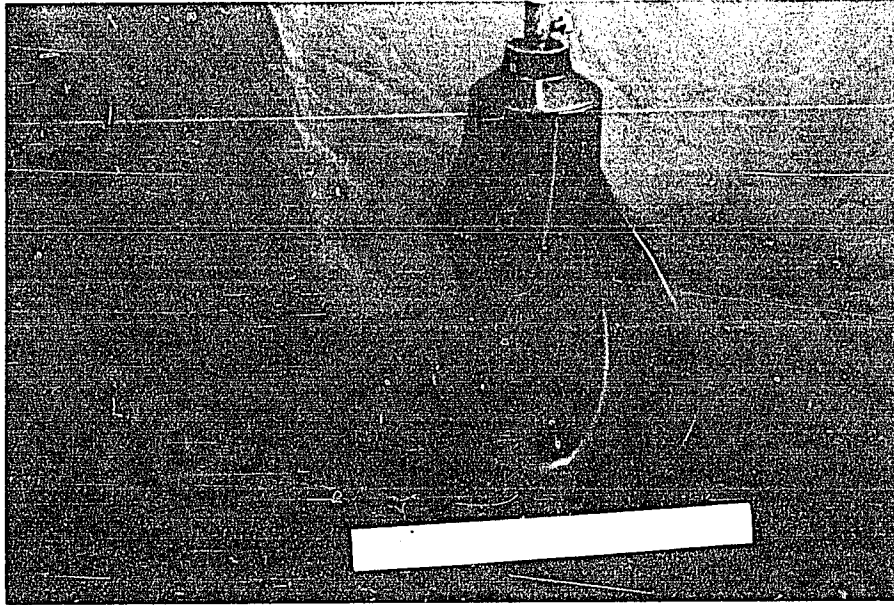


FIGURE 12. THREE-VANE WASHING MACHINE AGITATOR USED AS PROPELLER WITH THE BATCH PLANT SYSTEM

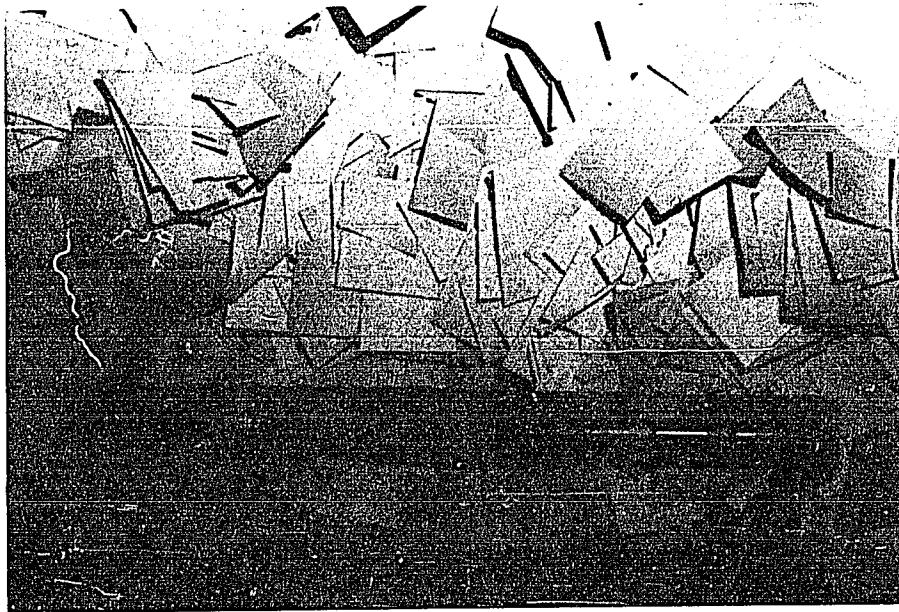


FIGURE 13. VARIOUS SHAPES AND SIZES OF UNBLEACHED PAPER CHIPS USED WITH THE BATCH PLANT SYSTEM

kraft sacks.

To determine the amount of papers which had wet and sunk to the tank bottom, a means had to be developed to collect and remove the wetted chips efficiently. Four baskets, made from interlocking nylon mesh, were constructed for this purpose. The material was non-reactive with the surfactant and had openings of about 1/8 inch which drained well and did not interfere with flow. The baskets had the same dimensions as the inside of the tank with approximately three inches of extra material protruding over the tank top for attachment. The bottom of the baskets was held taut with stainless steel rods formed to the tank bottom dimensions.

A picture of various components of this mixed demonstration system is shown in Figure 14. This picture shows the plexiglass tank, variable speed motor, propeller, and the mesh baskets placed inside the tank. The physical dimensions are shown in Figure 15.

#### Procedures for Operating Mixed Batch System

When the components of the apparatus were in position, the tank was filled with 500 liters of tap water. After the surfactant was added, the mixer was used to disperse it throughout the tank. Excess foaming was not a problem since only low concentrations of surfactants were used.

The control on the mixer was set at a desired speed and frequently checked visually with an electric timer. The papers that were then added had been weighed on a pan balance calibrated to 0.1 grams. The

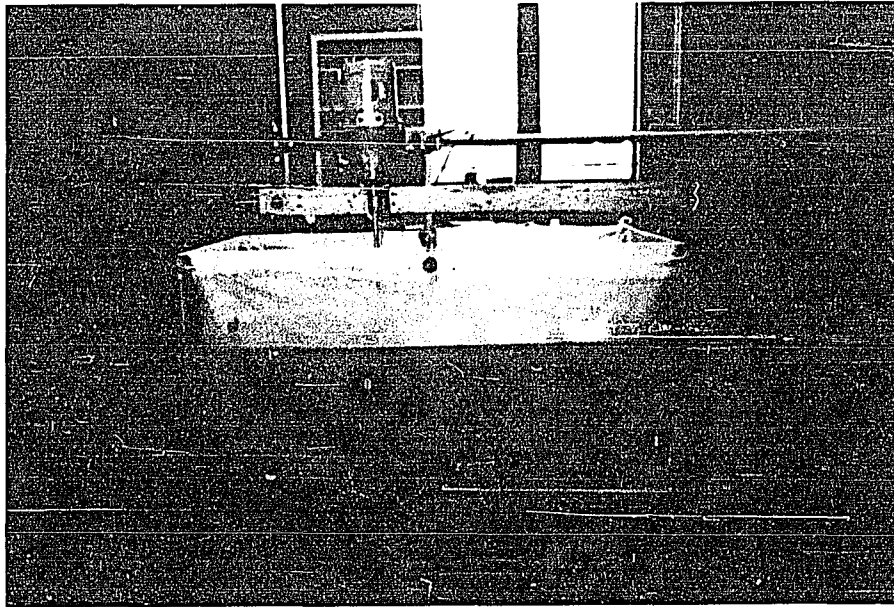


FIGURE 14 TANK, MOTOR, PROPELLER, AND MESH BASKET USED IN PAPER RECOVERY PROCESS WITH THE BATCH PLANT SYSTEM



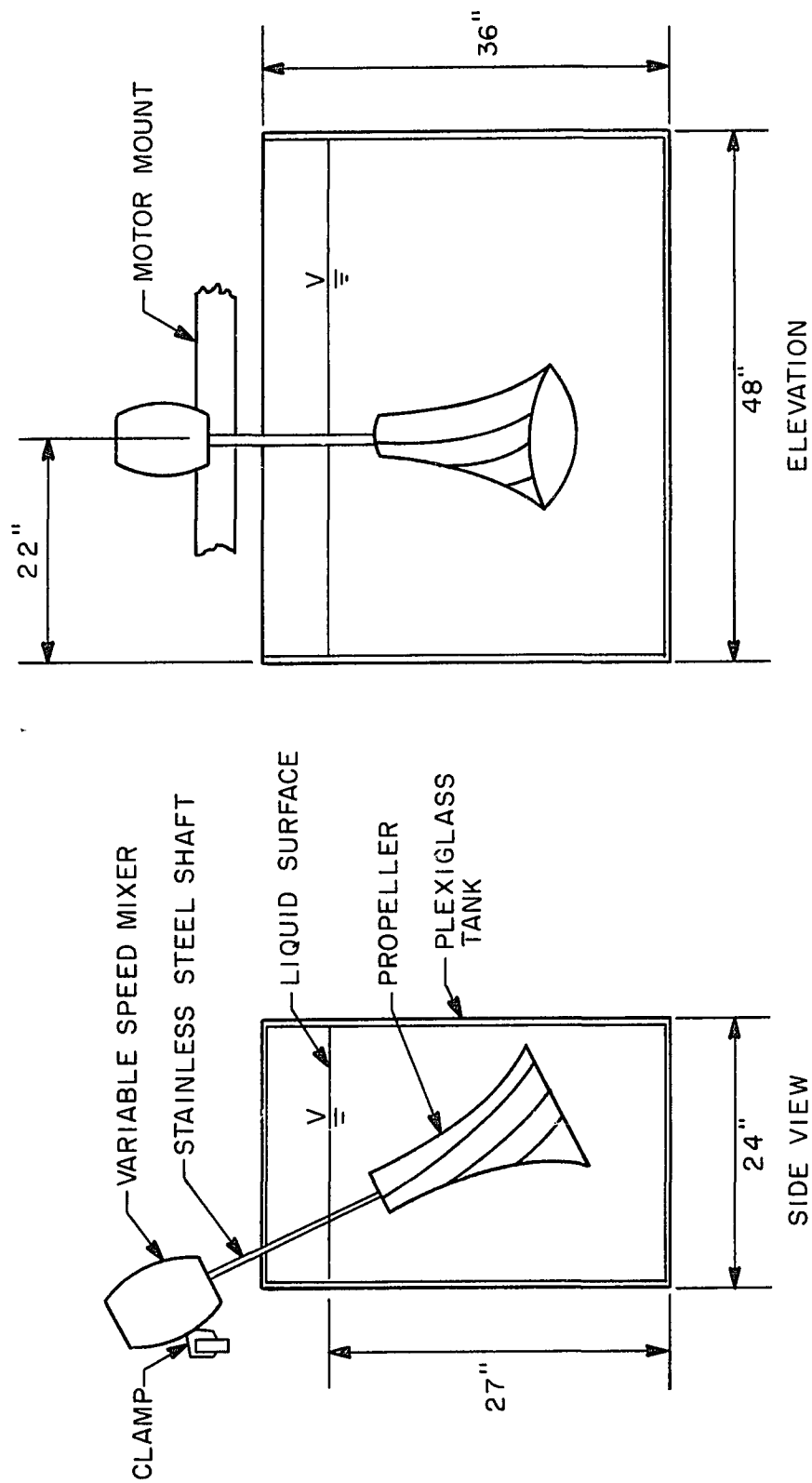


FIGURE 15. TANK AND MOTOR ARRANGEMENT USED IN PAPER RECOVERY PROCESS WITH THE BATCH PLANT SYSTEM

batch of papers was scattered over the tank and forced by hand below the liquid surface to accelerate the wetting on both sides and reduce initial paper sandwiching.

At a specified observation time the motor was turned off and the propeller was removed. The liquid was left undisturbed for approximately 30 seconds to allow wetted chips to sink to the bottom. The top mesh basket was disconnected from its clamps and one of its ends was slowly lowered below the floating papers. This end was carefully drawn across the tank to the other side in order to collect the settled papers. The top basket was then withdrawn from the tank. The papers that were still floating were only slightly disturbed in this operation. The propeller was reattached and the motor was set to the desired mixing speed. The mixing was uninterrupted until the next observation time. This operation required a total of five minutes for each observation to disconnect the propeller, remove the next bag, and, then, reconnect the propeller. Because four baskets were used, a total of five observations could be made to determine the quantities of paper recovered for each batch.

The contents of the basket were hand-sorted to separate bleached from unbleached papers when required. The chips were oven dried at 105°C and, then, weighed to determine the amount of papers recovered at each observation time.

The tank, propeller, and nylon baskets were washed with water between different loadings to remove any surfactant traces. The laboratory temperature averaged 65°F.

#### IV RESULTS

##### QUIESCENT DETENTION TIMES AND PAPER GRADE RECOVERY

The effect of water, cationic, anionic, and non-ionic surfactants on the recovery of the different grades of paper was investigated to develop a new paper recycling process.

##### Water

Ten paper chips for each of the samples were placed in deionized water to determine the detention times required for them to sink. The results using one-inch samples are shown in Table 10. The values recorded in the table represent the number of paper chips that remained floating at the observation time. In the case of the starch sized groundwood, it can be seen that two chips sank in 15 minutes and all ten sank in 72 hours. For the catalog and textweb groundwoods, wetting and sinking occurred almost immediately. This table shows that none of the coated foodboard chips or those from the wet-strength unbleached sacks sank in seven days. The detention times for all of the other paper samples can be seen to vary primarily from 72 to 96 hours when most of the chips can be recovered from the tank bottom.

##### Cationic Surfactants

Several long-chain cationic surfactants were studied to determine

| Paper<br>Sample | Time (Hours) |     |     |     |     |    |    |    |    |    |    |    |    |    |    |
|-----------------|--------------|-----|-----|-----|-----|----|----|----|----|----|----|----|----|----|----|
|                 | 0            | .25 | .50 | 1.0 | 1.5 | 3  | 3  | 1  | 0  | -  | -  | -  | -  | -  | -  |
| Printing        | 10           | 8   | 6   | 6   | 3   | 3  | 3  | 1  | 0  | -  | -  | -  | -  | -  | -  |
| Catalog         | 0            | -   | -   | -   | -   | -  | -  | -  | -  | -  | -  | -  | -  | -  | -  |
| Textweb         | 0            | -   | -   | -   | -   | -  | -  | -  | -  | -  | -  | -  | -  | -  | -  |
| Reg-str.        | 10           | 10  | 10  | 10  | 10  | 10 | 10 | 10 | 1  | 0  | -  | -  | -  | -  | -  |
| Wet-str.        | 10           | 10  | 10  | 10  | 10  | 10 | 10 | 10 | 4  | 0  | -  | -  | -  | -  | -  |
| Foodboard       | 10           | 10  | 10  | 10  | 10  | 10 | 10 | 10 | 10 | 10 | 10 | 10 | 10 | 10 | 10 |
| 40-lb           | 10           | 10  | 10  | 10  | 10  | 10 | 10 | 10 | 8  | 5  | 5  | 5  | 5  | 2  | 2  |
| 50-lb           | 10           | 10  | 10  | 10  | 10  | 10 | 10 | 10 | 10 | 10 | 10 | 10 | 10 | 10 | 10 |
| 60-lb           | 10           | 10  | 10  | 10  | 10  | 10 | 10 | 10 | 7  | 7  | 7  | 7  | 7  | 7  | 7  |
| Bond            | 10           | 10  | 10  | 10  | 10  | 10 | 10 | 10 | 0  | -  | -  | -  | -  | -  | -  |

TABLE 10. DETENTION TIMES REQUIRED TO RECOVER TEN PAPER CHIPS USING WATER

detention times and recovery groups for the paper samples. The selected surfactants had been used as emulsifiers, lubricants, and dispersing agents in related fiber industries. A brief description of the ones chosen from this group are listed in Table 9 giving their chemical class name and formula.

The detention times were observed for each sample using various concentrations of all the surfactants. The concentrations that were studied included 0.005, 0.01, 0.05, 0.1, 0.5, 1.0, and 2.0 percent for the different surfactants. The results are shown in Tables 11 to 15.

The detention times of the paper samples, using a dilute concentration of the quaternary ammonium salt are shown in Table 11. This table shows that 30 minutes are required to remove all the ground-wood papers from all the other non-groundwood samples. The bleached multiwall shipping sack with a wet-strength additive begins to separate from the mixture in 30 minutes and can be fully recovered in 1.75 hours. Its regular-strength counterpart can be removed in 2.5 hours. The sulphite bond paper has detention times between 1.25 and 1.75 hours. All of the unbleached samples have detention times from 3.0 to 10.0 hours for total recovery.

Table 12 shows the wetting results for this same surfactant as the concentration is increased from 0.01 to 0.1 percent. At this concentration all the groundwoods can be recovered in ten minutes instead of the previous 30 minutes. The detention times of the bleached kraft samples is lowered to between ten minutes and 1.5 hours.

| Paper<br>Sample | Time (Hours) |     |     |     |      |     |      |     |     |     |     |     |     |     |     |     |    |
|-----------------|--------------|-----|-----|-----|------|-----|------|-----|-----|-----|-----|-----|-----|-----|-----|-----|----|
|                 | 0            | .33 | .50 | .75 | 1.25 | 1.5 | 1.75 | 2.0 | 2.5 | 3.0 | 3.5 | 4.0 | 5.0 | 6.0 | 7.0 | 8.0 | 10 |
| Printing        | 10           | 10  | 0   | -   | -    | -   | -    | -   | -   | -   | -   | -   | -   | -   | -   | -   | -  |
| Catalog         | 0            | -   | -   | -   | -    | -   | -    | -   | -   | -   | -   | -   | -   | -   | -   | -   | -  |
| Textweb         | 0            | -   | -   | -   | -    | -   | -    | -   | -   | -   | -   | -   | -   | -   | -   | -   | -  |
| Reg-str.        | 10           | 10  | 10  | 10  | 8    | 8   | 7    | 3   | 0   | -   | -   | -   | -   | -   | -   | -   | -  |
| Wet-str.        | 10           | 10  | 9   | 7   | 5    | 5   | 0    | -   | -   | -   | -   | -   | -   | -   | -   | -   | -  |
| Foodboard       | 10           | 10  | 10  | 10  | 10   | 10  | 10   | 10  | 10  | 10  | 10  | 10  | 10  | 9   | 8   | 8   | 0  |
| 40-lb           | 10           | 10  | 10  | 10  | 10   | 10  | 10   | 10  | 10  | 9   | 5   | 1   | 0   | -   | -   | -   | -  |
| 50-lb           | 10           | 10  | 10  | 10  | 10   | 10  | 10   | 10  | 10  | 10  | 10  | 10  | 10  | 9   | 6   | 3   | 0  |
| 60-lb           | 10           | 10  | 10  | 10  | 10   | 10  | 10   | 10  | 10  | 10  | 10  | 10  | 8   | 3   | 1   | 0   | -  |
| Bond            | 10           | 10  | 10  | 10  | 4    | 2   | 0    | -   | -   | -   | -   | -   | -   | -   | -   | -   | -  |

TABLE 11. DETENTION TIMES REQUIRED TO RECOVER TEN PAPER CHIPS USING 0.01% QUATERNARY AMMONIUM SALT SURFACTANT

| Paper<br>Sample | Time (Hours) |      |      |     |     |    |     |     |      |     |     |    |
|-----------------|--------------|------|------|-----|-----|----|-----|-----|------|-----|-----|----|
|                 | 0            | .083 | .167 | .25 | .33 | .5 | .75 | 1.0 | 1.25 | 1.5 | 6.0 |    |
| Printing        | 10           | 7    | 0    | -   | -   | -  | -   | -   | -    | -   | -   | -  |
| Catalog         | 0            | -    | -    | -   | -   | -  | -   | -   | -    | -   | -   | -  |
| Textweb         | 0            | -    | -    | -   | -   | -  | -   | -   | -    | -   | -   | -  |
| Reg-str.        | 10           | 10   | 10   | 10  | 10  | 10 | 6   | 4   | 2    | 0   | -   | -  |
| Wet-str.        | 10           | 10   | 1    | 0   | -   | -  | -   | -   | -    | -   | -   | -  |
| Foodboard       | 10           | 10   | 10   | 10  | 10  | 10 | 10  | 10  | 10   | 10  | 10  | 10 |
| 40-lb           | 9            | 9    | 0    | -   | -   | -  | -   | -   | -    | -   | -   | -  |
| 50-lb           | 10           | 10   | 10   | 10  | 9   | 0  | -   | -   | -    | -   | -   | -  |
| 60-lb           | 10           | 10   | 10   | 10  | 9   | 0  | -   | -   | -    | -   | -   | -  |
| Bond            | 10           | 10   | 10   | 9   | 7   | 5  | 0   | -   | -    | -   | -   | -  |

TABLE 12. DETENTION TIMES REQUIRED TO RECOVER TEN PAPER CHIPS USING 0.1% QUATERNARY AMMONIUM SALT SURFACTANT

| Paper<br>Sample | Times (Hours) |     |    |     |    |      |      |    |      |     |    |     |    |   |   |
|-----------------|---------------|-----|----|-----|----|------|------|----|------|-----|----|-----|----|---|---|
|                 | 0             | .33 | .5 | .75 | 1  | 1.25 | 1.75 | 2  | 2.25 | 2.5 | 4  | 4.5 | 5  | 6 | 7 |
| Printing        | 10            | 0   | -  | -   | -  | -    | -    | -  | -    | -   | -  | -   | -  | - | - |
| Catalog         | 0             | -   | -  | -   | -  | -    | -    | -  | -    | -   | -  | -   | -  | - | - |
| Textweb         | 0             | -   | -  | -   | -  | -    | -    | -  | -    | -   | -  | -   | -  | - | - |
| Reg-str.        | 10            | 10  | 10 | 9   | 9  | 0    | -    | -  | -    | -   | -  | -   | -  | - | - |
| Wet-str.        | 10            | 10  | 8  | 5   | 0  | -    | -    | -  | -    | -   | -  | -   | -  | - | - |
| Foodboard       | 10            | 10  | 10 | 10  | 10 | 10   | 10   | 10 | 10   | 10  | 10 | 10  | 10 | 8 | 0 |
| 40-lb           | 10            | 10  | 10 | 10  | 10 | 10   | 9    | 6  | 4    | 0   | -  | -   | -  | - | - |
| 50-lb           | 10            | 10  | 10 | 10  | 10 | 10   | 10   | 10 | 10   | 10  | 9  | 9   | 8  | 0 | - |
| 60-lb           | 10            | 10  | 10 | 10  | 10 | 10   | 10   | 10 | 10   | 10  | 8  | 6   | 3  | 0 | - |
| Bond            | 10            | 9   | 8  | 2   | 0  | -    | -    | -  | -    | -   | -  | -   | -  | - | - |

TABLE 13. DETENTION TIMES REQUIRED TO RECOVER TEN PAPER CHIPS USING 0.01%  
HETEROCYCLIC TERTIARY AMINE SURFACTANT



| Paper<br>Sample | Time (Hours) |     |    |     |    |      |     |      |    |     |    |    |    |     |   |     |   |    |
|-----------------|--------------|-----|----|-----|----|------|-----|------|----|-----|----|----|----|-----|---|-----|---|----|
|                 | 0            | .33 | .5 | .75 | 1  | 1.25 | 1.5 | 1.75 | 2  | 2.5 | 3  | 5  | 6  | 6.5 | 7 | 7.5 | 8 | 10 |
| Printing        | 10           | 6   | 0  | -   | -  | -    | -   | -    | -  | -   | -  | -  | -  | -   | - | -   | - | -  |
| Catalog         | 0            | -   | -  | -   | -  | -    | -   | -    | -  | -   | -  | -  | -  | -   | - | -   | - | -  |
| Textweb         | 0            | -   | -  | -   | -  | -    | -   | -    | -  | -   | -  | -  | -  | -   | - | -   | - | -  |
| Reg-str.        | 10           | 10  | 10 | 10  | 9  | 8    | 5   | 1    | 0  | -   | -  | -  | -  | -   | - | -   | - | -  |
| Wet-str.        | 10           | 8   | 2  | 1   | 0  | -    | -   | -    | -  | -   | -  | -  | -  | -   | - | -   | - | -  |
| Foodboard       | 10           | 10  | 10 | 10  | 10 | 10   | 10  | 10   | 10 | 10  | 10 | 10 | 10 | 10  | 9 | 5   | 4 | 0  |
| 40-lb           | 10           | 10  | 10 | 10  | 10 | 8    | 8   | 6    | 4  | 1   | 0  | -  | -  | -   | - | -   | - | -  |
| 50-lb           | 10           | 10  | 10 | 10  | 10 | 10   | 10  | 10   | 10 | 10  | 10 | 9  | 8  | 7   | 3 | 2   | 0 | -  |
| 60-lb           | 10           | 10  | 10 | 10  | 10 | 10   | 10  | 10   | 10 | 10  | 9  | 7  | 3  | 2   | 1 | 0   | - | -  |
| Bond            | 10           | 10  | 10 | 9   | 4  | 0    | -   | -    | -  | -   | -  | -  | -  | -   | - | -   | - | -  |

TABLE 14. DETENTION TIMES REQUIRED TO RECOVER TEN PAPER CHIPS USING 1.0% CETYL PYRIDINIUM CHLORIDE SURFACTANT

| Paper<br>Sample | Times (Hours) |     |     |    |     |    |      |     |      |     |      |      |    |     |     |     |   |      |    |
|-----------------|---------------|-----|-----|----|-----|----|------|-----|------|-----|------|------|----|-----|-----|-----|---|------|----|
|                 | 0             | .16 | .33 | .5 | .75 | 1  | 1.25 | 1.5 | 2.25 | 2.5 | 2.75 | 3.25 | 4  | 4.5 | 6.5 | 8.5 | 9 | 10.5 | 11 |
| Printing        | 10            | 7   | 0   | -  | -   | -  | -    | -   | -    | -   | -    | -    | -  | -   | -   | -   | - | -    | -  |
| Catalog         | 0             | -   | -   | -  | -   | -  | -    | -   | -    | -   | -    | -    | -  | -   | -   | -   | - | -    | -  |
| Textweb         | 0             | -   | -   | -  | -   | -  | -    | -   | -    | -   | -    | -    | -  | -   | -   | -   | - | -    | -  |
| Reg-str.        | 10            | 10  | 10  | 10 | 10  | 9  | 3    | 0   | -    | -   | -    | -    | -  | -   | -   | -   | - | -    | -  |
| Wet-str.        | 10            | 10  | 8   | 7  | 0   | -  | -    | -   | -    | -   | -    | -    | -  | -   | -   | -   | - | -    | -  |
| Foodboard       | 10            | 10  | 10  | 10 | 10  | 10 | 10   | 10  | 10   | 10  | 10   | 10   | 10 | 10  | 7   | 3   | 1 | 0    | -  |
| 40-lb           | 10            | 10  | 10  | 10 | 10  | 10 | 10   | 10  | 9    | 5   | 4    | 2    | 1  | 0   | -   | -   | - | -    | -  |
| 50-lb           | 10            | 10  | 10  | 10 | 10  | 10 | 10   | 10  | 10   | 10  | 10   | 10   | 10 | 10  | 10  | 8   | 8 | 3    | 0  |
| 60-lb           | 10            | 10  | 10  | 10 | 10  | 10 | 10   | 10  | 10   | 10  | 10   | 10   | 9  | 9   | 8   | 5   | 4 | 1    | 0  |
| Bond            | 10            | 10  | 10  | 7  | 3   | 1  | 0    | -   | -    | -   | -    | -    | -  | -   | -   | -   | - | -    | -  |

TABLE 15. DETENTION TIMES REQUIRED TO RECOVER TEN PAPER CHIPS USING 0.01%  
FATTY AMINE AND SORBITOL OLEATE SURFACTANT

Most of the unbleached sacks require only 20 to 30 minutes to totally wet and sink, while the bleached sulphite can all be recovered in 45 minutes.

Table 13 shows the detention times and recovery groups which can be achieved with a dilute concentration of heterocyclic tertiary amine. At the 0.01% concentration, all groundwoods are removed from non-groundwoods in only 20 minutes. The bleached papers separated from the unbleached by sinking out in 1.25 hours. This is still 30 minutes before the first unbleached sample begins to wet. Furthermore, while all the uncoated papers can be seen to sink between the fifth and sixth hour, most of the coated foodboard chips are still floating on the surface.

The results of the wetting and sinking times using a 1.0% cetyl pyridinium chloride for the samples are shown in Table 14; those for another cationic, a polyoxyethylene combination fatty amine and sorbitol oleate, are included in Table 15. The results can be similarly interpreted as were done for those using the other surfactants. As would be expected different detention times were found for the different recovery groups.

#### Anionic Surfactants

Several anionic surfactants were selected to determine their effects on lowering the detention times of the paper samples compared to that of water and determine if desirable recovery groups would be possible. These synthetic detergents were all long chained hydrocarbons to which a negatively charged sulfo group had been attached. A

brief description of the specific syndets used for this study is included in Table 9 which gives their chemical class name and formula. These particular surfactants have found many uses in related fields as excellent wetting and penetrating agents.

As performed for the cationic surfactants, the detention times were observed and recorded for all the paper samples with several concentrations for each of these surfactants. The range of concentrations included 0.005, 0.01, 0.05, 0.1, 0.5, and 1.0 percent diluted with deionized water. Selected results are shown in Tables 16 to 19.

Table 16 shows the results of the detention times for the paper samples when a 0.05% solution of a sulfated fatty acid ester was used as a wetting agent. It can be seen that in ten minutes all the groundwoods have sunk to the bottom while all other papers remain floating. The next paper which wets and separates is the lightest unbleached kraft sack, which entirely sinks in two hours. This is followed by the bleached bond paper which entirely sinks in 2.5 hours. The majority of the unbleached papers have sunk by the sixth hour; the bleached, by the tenth. The coated foodboard chips floated on the surface for three days before they wetted and sank.

Table 17 shows the results of the detention times when a dilute solution of alkyl aryl sulfonate was used as a wetting agent. All of the groundwoods can be recovered in a detention time of 20 minutes. The next paper which wets and sinks is the bleached bond. Further examination indicated that most of the unbleached kraft sacks can be

| Paper<br>Sample | Time (Hours) |     |     |     |      |     |    |      |     |    |     |    |     |    |    |    |
|-----------------|--------------|-----|-----|-----|------|-----|----|------|-----|----|-----|----|-----|----|----|----|
|                 | 0            | .16 | .33 | .75 | 1.25 | 1.5 | 2  | 2.25 | 2.5 | 3  | 3.5 | 4  | 4.5 | 5  | 6  | 7  |
| Printing        | 10           | 0   | -   | -   | -    | -   | -  | -    | -   | -  | -   | -  | -   | -  | -  | -  |
| Catalog         | 0            | -   | -   | -   | -    | -   | -  | -    | -   | -  | -   | -  | -   | -  | -  | -  |
| Textweb         | 0            | -   | -   | -   | -    | -   | -  | -    | -   | -  | -   | -  | -   | -  | -  | -  |
| Reg-str.        | 10           | 10  | 10  | 10  | 10   | 10  | 10 | 10   | 10  | 10 | 10  | 10 | 10  | 10 | 8  | 6  |
| Wet-str.        | 10           | 10  | 9   | 9   | 9    | 9   | 8  | 7    | 7   | 7  | 7   | 6  | 6   | 4  | 4  | 0  |
| Foodboard       | 10           | 10  | 10  | 10  | 10   | 10  | 10 | 10   | 10  | 10 | 10  | 10 | 10  | 10 | 10 | 10 |
| 40-lb           | 10           | 9   | 9   | 6   | 4    | 4   | 0  | -    | -   | -  | -   | -  | -   | -  | -  | -  |
| 50-lb           | 10           | 10  | 10  | 10  | 10   | 10  | 10 | 10   | 10  | 10 | 10  | 10 | 10  | 8  | 8  | 4  |
| 60-lb           | 10           | 10  | 10  | 10  | 10   | 10  | 9  | 9    | 9   | 8  | 7   | 7  | 6   | 3  | 0  | -  |
| Bond            | 10           | 10  | 10  | 8   | 6    | 5   | 3  | 1    | 0   | -  | -   | -  | -   | -  | -  | -  |

TABLE 16. DETENTION TIMES REQUIRED TO RECOVER TEN PAPER CHIPS USING 0.05% SULFATED FATTY ACID ESTER SURFACTANT

| Paper<br>Sample | Time (Hours) |     |     |     |      |     |      |     |     |     |     |     |     |     |     |       |
|-----------------|--------------|-----|-----|-----|------|-----|------|-----|-----|-----|-----|-----|-----|-----|-----|-------|
|                 | 0            | .16 | .33 | 1.0 | 1.25 | 1.5 | 1.75 | 2.0 | 2.5 | 3.0 | 3.5 | 4.0 | 6.0 | 7.0 | 8.0 | 24    |
| Printing        | 10           | 3   | 0   | -   | -    | -   | -    | -   | -   | -   | -   | -   | -   | -   | -   | -     |
| Catalog         | 0            | -   | -   | -   | -    | -   | -    | -   | -   | -   | -   | -   | -   | -   | -   | -     |
| Textweb         | 0            | -   | -   | -   | -    | -   | -    | -   | -   | -   | -   | -   | -   | -   | -   | -     |
| Reg-str.        | 10           | 10  | 10  | 10  | 10   | 10  | 10   | 10  | 10  | 10  | 10  | 10  | 10  | 10  | 10  | 3 0   |
| Wet-str.        | 10           | 10  | 10  | 10  | 10   | 10  | 10   | 10  | 10  | 10  | 9   | 9   | 6   | 6   | 5 5 | 0 -   |
| Foodboard       | 10           | 10  | 10  | 10  | 10   | 10  | 10   | 10  | 10  | 10  | 10  | 10  | 10  | 10  | 10  | 10 10 |
| 40-lb           | 10           | 10  | 10  | 10  | 10   | 10  | 10   | 9   | 8   | 5   | 2   | 0   | -   | -   | -   | -     |
| 50-lb           | 10           | 10  | 10  | 10  | 10   | 10  | 10   | 10  | 10  | 10  | 10  | 10  | 10  | 8   | 8 6 | 0 -   |
| 60-lb           | 10           | 10  | 10  | 10  | 10   | 10  | 10   | 10  | 10  | 10  | 10  | 9   | 3   | 1   | 0   | - -   |
| Bond            | 10           | 10  | 10  | 9   | 7    | 5   | 4    | 3   | 0   | -   | -   | -   | -   | -   | -   | -     |

TABLE 17. DETENTION TIMES REQUIRED TO RECOVER TEN PAPER CHIPS USING 0.01%  
ALKYL ARYL SULFONATE (ABS) SURFACTANT

| Paper<br>Sample | Time (Hours) |     |     |    |     |     |    |     |    |    |    |    |    |    |   |   |
|-----------------|--------------|-----|-----|----|-----|-----|----|-----|----|----|----|----|----|----|---|---|
|                 | 0            | .16 | .34 | .5 | 1.5 | 2.5 | 3  | 3.5 | 4  | 5  | 10 | 12 | 24 | 48 |   |   |
| Printing        | 10           | 9   | 2   | 0  | -   | -   | -  | -   | -  | -  | -  | -  | -  | -  | - | - |
| Catalog         | 0            | -   | -   | -  | -   | -   | -  | -   | -  | -  | -  | -  | -  | -  | - | - |
| Textweb         | 0            | -   | -   | -  | -   | -   | -  | -   | -  | -  | -  | -  | -  | -  | - | - |
| Reg-str.        | 10           | 10  | 10  | 10 | 10  | 10  | 10 | 10  | 10 | 10 | 10 | 10 | 1  | 0  |   |   |
| Wet-str.        | 10           | 10  | 10  | 10 | 10  | 10  | 10 | 10  | 10 | 10 | 8  | 3  | 0  | -  |   |   |
| Foodboard       | 10           | 10  | 10  | 10 | 10  | 10  | 10 | 10  | 10 | 10 | 10 | 10 | 10 | 9  |   |   |
| 40-lb           | 10           | 10  | 10  | 10 | 9   | 9   | 7  | 5   | 2  | 0  | -  | -  | -  | -  |   |   |
| 50-lb           | 10           | 10  | 10  | 10 | 10  | 10  | 10 | 10  | 10 | 10 | 10 | 2  | 0  | -  |   |   |
| 60-lb           | 10           | 10  | 10  | 10 | 10  | 10  | 10 | 10  | 10 | 10 | 6  | 0  | -  | -  |   |   |
| Bond            | 10           | 10  | 10  | 7  | 7   | 5   | 0  | -   | -  | -  | -  | -  | -  | -  |   |   |

TABLE 18. DETENTION TIMES REQUIRED TO RECOVER TEN PAPER CHIPS USING 0.01% SODIUM LAURYL ETHER SULFATE SURFACTANT

| Paper<br>Sample | 0  | .16 | Time (Hours) |     |      |    |     |     |     |     |     |     |     |    |    |    |  |  |  |  |
|-----------------|----|-----|--------------|-----|------|----|-----|-----|-----|-----|-----|-----|-----|----|----|----|--|--|--|--|
|                 |    |     | 1.25         | 1.5 | 1.75 | 2  | 2.5 | 3.0 | 3.5 | 4.0 | 4.5 | 5.0 | 7.0 | 12 | 20 | 24 |  |  |  |  |
| Printing        | 10 | 0   | -            | -   | -    | -  | -   | -   | -   | -   | -   | -   | -   | -  | -  | -  |  |  |  |  |
| Catalog         | 0  | -   | -            | -   | -    | -  | -   | -   | -   | -   | -   | -   | -   | -  | -  | -  |  |  |  |  |
| Textweb         | 0  | -   | -            | -   | -    | -  | -   | -   | -   | -   | -   | -   | -   | -  | -  | -  |  |  |  |  |
| Reg-str.        | 10 | 10  | 10           | 10  | 10   | 10 | 10  | 10  | 9   | 8   | 8   | 8   | 8   | 6  | 0  | -  |  |  |  |  |
| Wet-str.        | 10 | 10  | 10           | 10  | 10   | 9  | 8   | 8   | 6   | 5   | 3   | 1   | 1   | 0  | -  | -  |  |  |  |  |
| Foodboard       | 10 | 10  | 10           | 10  | 10   | 10 | 10  | 10  | 10  | 10  | 10  | 10  | 10  | 10 | 10 | 10 |  |  |  |  |
| 40-lb           | 10 | 10  | 10           | 8   | 8    | 8  | 7   | 2   | 1   | 0   | -   | -   | -   | -  | -  | -  |  |  |  |  |
| 50-lb           | 10 | 10  | 10           | 10  | 10   | 10 | 10  | 10  | 10  | 10  | 10  | 10  | 10  | 8  | 0  | -  |  |  |  |  |
| 60-lb           | 10 | 10  | 10           | 10  | 10   | 10 | 10  | 10  | 9   | 9   | 9   | 9   | 8   | 6  | 0  | -  |  |  |  |  |
| Bond            | 10 | 10  | 9            | 8   | 6    | 4  | 3   | 0   | -   | -   | -   | -   | -   | -  | -  | -  |  |  |  |  |

TABLE 19. DETENTION TIMES REQUIRED TO RECOVER TEN PAPER CHIPS USING 0.01% SULFATED ALKYLPHENOL POLYGLYCOL ETHER SURFACTANT



removed in ten hours, while twenty hours are needed for the bleached samples. All of the cup sidewall chips require a detention time longer than two days before sinking is accomplished.

The results using a 0.01% sodium lauryl ether sulfate can be seen in Table 18. The last anionic surfactant used was an alkylphenol polyglycol ether. The results for the 0.01% concentration are included in Table 19. The detention times are presented for each of the paper grades for these identical concentrations.

#### Non-ionic Surfactants

Three non-ionic syndets, all based on polyethylene, were used to determine the effects of accelerating and wetting of the selected paper samples and to determine if any desirable recovery groups could be achieved. These specific surfactants had been used extensively in emulsion and lubricating processes. Table 9 gives a detailed description of them along with their chemical formula.

As performed for the other ionic surfactants, these were diluted to form concentrations of 0.005, 0.01, 0.05, 0.1, 0.5, and 1.0 percent and used to measure the detention times of all the paper samples. Important selected results are found in Tables 20 to 22.

The dilute ether, shown in Table 20 resulted in the groundwoods sinking in 15 minutes leaving all remaining non-groundwoods still floating. After a detention time of 45 minutes, three dissimilar papers began to sink and separate from the others. These papers are the bleached wet-strength kraft and bond papers and the lightest unbleached kraft sack. The results at 1.75 hours show that by this time

| Paper<br>Sample | Time (Hours) |     |    |     |    |      |     |      |    |      |     |      |    |      |     |    |
|-----------------|--------------|-----|----|-----|----|------|-----|------|----|------|-----|------|----|------|-----|----|
|                 | 0            | .25 | .5 | .75 | 1  | 1.25 | 1.5 | 1.75 | 2  | 2.25 | 2.5 | 2.75 | 3  | 3.25 | 3.5 | 20 |
| Printing        | 10           | 0   | -  | -   | -  | -    | -   | -    | -  | -    | -   | -    | -  | -    | -   | -  |
| Catalog         | 0            | -   | -  | -   | -  | -    | -   | -    | -  | -    | -   | -    | -  | -    | -   | -  |
| Textweb         | 0            | -   | -  | -   | -  | -    | -   | -    | -  | -    | -   | -    | -  | -    | -   | -  |
| Reg-str.        | 10           | 10  | 10 | 10  | 10 | 10   | 9   | 7    | 6  | 3    | 3   | 2    | 2  | 0    | -   | -  |
| Wet-str.        | 10           | 10  | 9  | 9   | 8  | 6    | 1   | 0    | -  | -    | -   | -    | -  | -    | -   | -  |
| Foodboard       | 10           | 10  | 10 | 10  | 10 | 10   | 10  | 10   | 10 | 10   | 10  | 10   | 10 | 10   | 10  | 0  |
| 40-lb           | 10           | 10  | 9  | 4   | 0  | -    | -   | -    | -  | -    | -   | -    | -  | -    | -   | -  |
| 50-lb           | 10           | 10  | 10 | 10  | 10 | 9    | 9   | 9    | 9  | 8    | 8   | 7    | 5  | 3    | 0   | -  |
| 60-lb           | 10           | 10  | 10 | 10  | 10 | 10   | 10  | 10   | 10 | 9    | 8   | 1    | 1  | 0    | -   | -  |
| Bond            | 10           | 10  | 10 | 5   | 2  | 1    | 0   | -    | -  | -    | -   | -    | -  | -    | -   | -  |

TABLE 20. DETENTION TIMES REQUIRED TO RECOVER TEN PAPER CHIPS USING 0.01% POLYOXYETHYLENE TRIDECYL ETHER SURFACTANT

| Paper<br>Sample | Time (Hours) |     |     |    |    |      |     |      |    |    |    |     |    |     |    |
|-----------------|--------------|-----|-----|----|----|------|-----|------|----|----|----|-----|----|-----|----|
|                 | 0            | .15 | .33 | .5 | 1  | 1.25 | 1.5 | 1.75 | 2  | 3  | 4  | 4.5 | 5  | 4.5 | 6  |
| Printing        | 10           | 5   | 1   | 0  | -  | -    | -   | -    | -  | -  | -  | -   | -  | -   | -  |
| Catalog         | 0            | -   | -   | -  | -  | -    | -   | -    | -  | -  | -  | -   | -  | -   | -  |
| Textweb         | 0            | -   | -   | -  | -  | -    | -   | -    | -  | -  | -  | -   | -  | -   | -  |
| Reg-str.        | 10           | 10  | 10  | 10 | 10 | 10   | 10  | 10   | 10 | 10 | 10 | 10  | 8  | 7   | 7  |
| Wet-str.        | 10           | 10  | 10  | 10 | 9  | 8    | 8   | 7    | 7  | 4  | 3  | 3   | 2  | 1   | 0  |
| Foodboard       | 10           | 10  | 10  | 10 | 10 | 10   | 10  | 10   | 10 | 10 | 10 | 10  | 10 | 10  | 10 |
| 40-lb           | 10           | 10  | 7   | 0  | -  | -    | -   | -    | -  | -  | -  | -   | -  | -   | -  |
| 50-lb           | 10           | 10  | 10  | 10 | 10 | 10   | 10  | 10   | 10 | 9  | 7  | 7   | 5  | 5   | 2  |
| 60-lb           | 10           | 10  | 10  | 10 | 9  | 9    | 9   | 9    | 9  | 9  | 4  | 0   | -  | -   | -  |
| Bond            | 10           | 10  | 10  | 10 | 10 | 10   | 8   | 6    | 5  | 0  | -  | -   | -  | -   | -  |

TABLE 21. DETENTION TIMES REQUIRED TO RECOVER TEN PAPER CHIPS USING 0.05% POLYOXYETHYLENE SORBITAN MONOLAURATE SURFACTANT

| Paper<br>Sample | Time (Hours) |     |     |    |     |    |      |     |      |    |      |     |    |     |    |    |
|-----------------|--------------|-----|-----|----|-----|----|------|-----|------|----|------|-----|----|-----|----|----|
|                 | 0            | .16 | .33 | .5 | .75 | 1  | 1.25 | 1.5 | 1.75 | 2  | 2.25 | 2.5 | 3  | 3.5 | 4  | 24 |
| Printing        | 10           | 2   | 0   | -  | -   | -  | -    | -   | -    | -  | -    | -   | -  | -   | -  | -  |
| Catalog         | 0            | -   | -   | -  | -   | -  | -    | -   | -    | -  | -    | -   | -  | -   | -  | -  |
| Textweb         | 0            | -   | -   | -  | -   | -  | -    | -   | -    | -  | -    | -   | -  | -   | -  | -  |
| Reg-str.        | 10           | 10  | 10  | 10 | 10  | 10 | 10   | 9   | 6    | 5  | 0    | -   | -  | -   | -  | -  |
| Wet-str.        | 10           | 10  | 9   | 8  | 7   | 5  | 0    | -   | -    | -  | -    | -   | -  | -   | -  | -  |
| Foodboard       | 10           | 10  | 10  | 10 | 10  | 10 | 10   | 10  | 10   | 10 | 10   | 10  | 10 | 10  | 10 | 0  |
| 40-lb           | 10           | 10  | 4   | 2  | 0   | -  | -    | -   | -    | -  | -    | -   | -  | -   | -  | -  |
| 50-lb           | 10           | 10  | 10  | 10 | 10  | 10 | 10   | 10  | 10   | 10 | 10   | 9   | 9  | 7   | 0  | -  |
| 60-lb           | 10           | 10  | 9   | 9  | 9   | 8  | 8    | 8   | 6    | 5  | 4    | 4   | 0  | -   | -  | -  |
| Bond            | 9            | 8   | 8   | 8  | 5   | 5  | 2    | 0   | -    | -  | -    | -   | -  | -   | -  | -  |

TABLE 22. DETENTION TIMES REQUIRED TO RECOVER TEN PAPER CHIPS USING 0.05% POLYOXYETHYLENE COCONUT FATTY ACID SURFACTANT

most of the bleached kraft have wetted leaving most of the unbleached samples still on the surface. However, all of the other light unbleached chips have already sunk 45 minutes previously. All the coated paper chips are still floating after all the other samples have sunk.

The detention times required to recover the paper samples using dilute polyoxyethylene sorbitan monolaurate as the wetting agent are shown in Table 21. All groundwoods can be recovered in 30 minutes with the remaining other samples still floating. While some of the unbleached sacks can be removed in only twenty minutes, over six hours are required to entirely recover all the samples. The range of wetting for the bleached kraft detention times is between one and twenty hours.

The detention times required to recover the paper samples using a 0.05% concentration of a polyoxyethylene coconut fatty acid surfactant are shown in Table 22.

#### SURFACE TENSIONS

The surface tensions which are fundamental in all the wetting expressions were determined at concentrations of 0.01, 0.1, 1.0, and 5.0 percent for two ionic surfactants. The cationic surfactant was a quaternary ammonium derivative (Atlas G-3634A) and the anionic was an alkyl aryl sulfonate (Atlas G-3300).

The average of the surface tension values are listed in Table 23 for these different concentrations. The surface tension of water can

| <u>SURFACTANT</u>                        | <u>CONCENTRATION,<br/>percent</u> | <u>SURFACE TENSION,<br/>dynes/cm</u> |
|--|-----------------------------------|--------------------------------------|
| Cationic, quaternary ammonium derivative | 0.0                               | 72.8                                 |
|  | 0.01                              | 38                                   |
|  | 0.1                               | 37                                   |
|  | 1.0                               | 37                                   |
|  | 5.0                               | 35                                   |
| Anionic, alkyl aryl sulfonate            | 0.0                               | 72.8                                 |
|  | 0.01                              | 30                                   |
|  | 0.1                               | 29                                   |
|  | 1.0                               | 29                                   |
|  | 5.0                               | 29                                   |

TABLE 23. SURFACE TENSIONS OF SURFACE-ACTIVE AGENTS

be seen to be appreciably reduced by using dilute solutions of either the cationic or anionic surfactant. The value for pure water at 72.8 dynes/cm is lowered to 38 dynes/cm for the 0.01% cationic surfactant and to 30 dynes/cm at the same concentration with the anionic detergent. As the concentrations of the surfactants increased, the surface tension continues to decrease but reaches a plateau beyond which higher concentrations do not exceed. The surface tension of the cationic surfactant dropped from 38 to 35 dynes/cm as the concentration increased from 0.01 to 5.0%. The anionic detergent experienced a lowering from 30 to 29 dynes/cm as the concentration changed from 0.01 to 0.1% and this was not further altered as the concentration increased to 5.0%.

#### TRANSIENT CONTACT ANGLES

The transient contact angles were determined using water and various concentrations of a cationic and an anionic surfactant on all the paper samples. The cationic was a quaternary ammonium derivative (Atlas G-3634A) and the anionic was an alkyl aryl sulfonate (Atlas G-3300). The concentrations were 0.005, 0.01, 0.02, 0.075, and 0.25%.

Using the standard needle, the size of the drops in this study varied with the type and concentration of the surfactant. For the concentrations of the cationic surfactant the range of values varied between 0.011 and 0.017 ml; the anionic detergent exhibited a similar range between 0.013 and 0.020 ml. The drop volume of pure water was found to be about 0.021 ml. In agreement with other published works,<sup>(73)</sup>

varying the size of the drops on the substrate did not cause any significant change in the result.

#### Cationic Surfactant

The transient contact angles obtained for water and various concentrations of the cationic surfactant on all the individual paper samples are shown on Figures 16 to 25. The transient contact angles shown were extended past the five second time interval to establish the initial values.

The cationic transient wetting curves for all of the bleached groundwood paper samples are shown in Figures 16 to 18. By comparing these results some observations can be made. Figure 17 shows the wetting characteristics for the 30#(44.38 g/m<sup>2</sup>) catalog paper, also the thinnest (.076 mm), which had been internally sized with rosin. The contact angle, when water was used as the wetting agent, decreased rapidly, from an initial value of 62.5° to less than 10° in only 100 seconds, and disappeared altogether in less than 120 seconds. Wetting with the different concentrations of the surfactant showed even faster wetting. Figure 18 shows the results achieved with water and the same wetting agent concentrations on the 38#(56.22 g/m<sup>2</sup>) groundwood paper sample which, in addition to being internally sized with rosin, had been clay coated. The initial contact angle with water decreased from an initial 71° to 50° by 120 seconds, while more rapid wetting occurred as the surfactant concentrations increased. The surface wetting of the last groundwood is shown on Figure 16. This externally starch sized sample with a 45#(66.6 g/m<sup>2</sup>) basis weight and



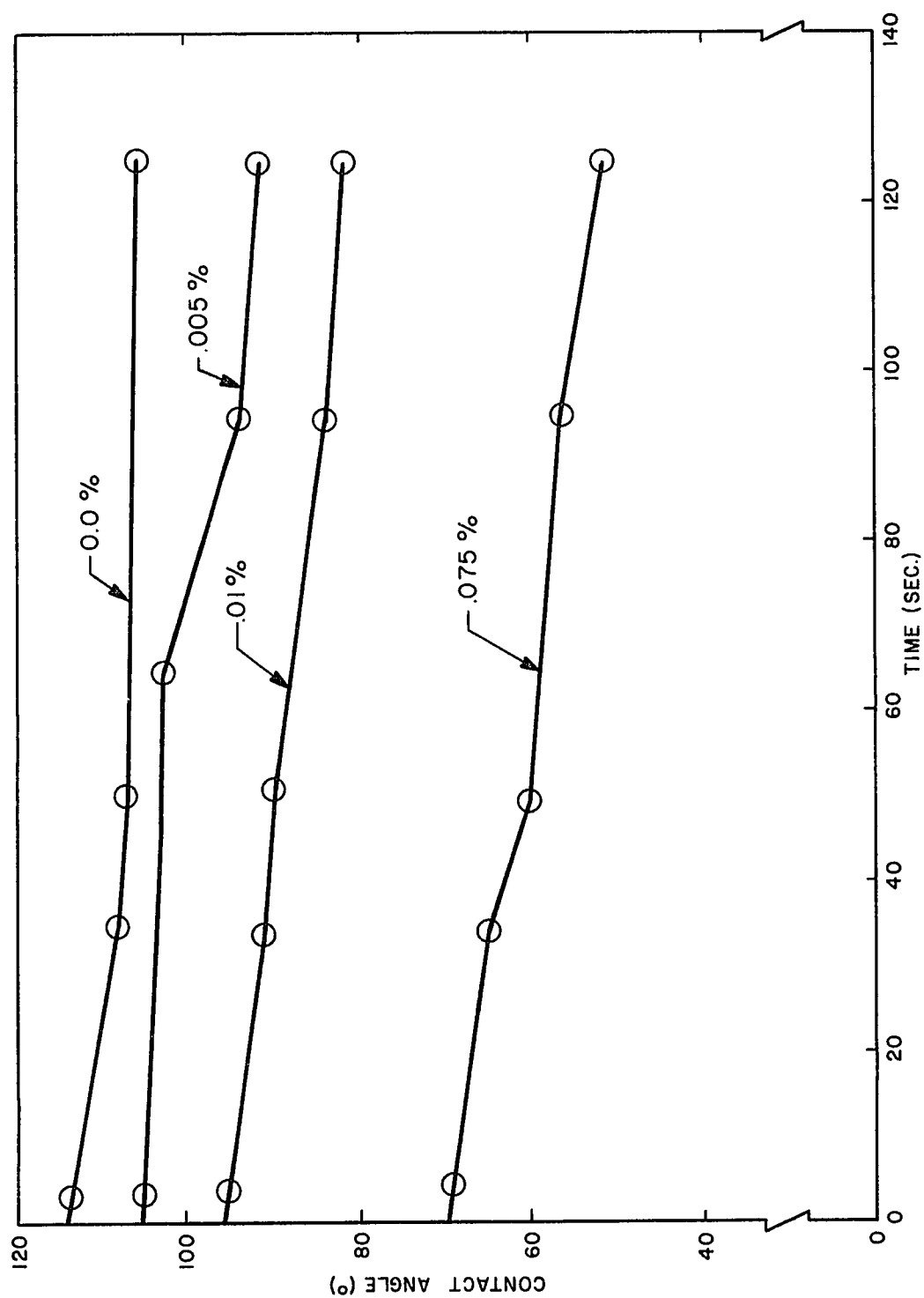


FIGURE 16. TRANSIENT CONTACT ANGLES OF 45-LB, BLEACHED, STARCH SIZED GROUNDWOOD WITH QUATERNARY AMMONIA SURFACTANT

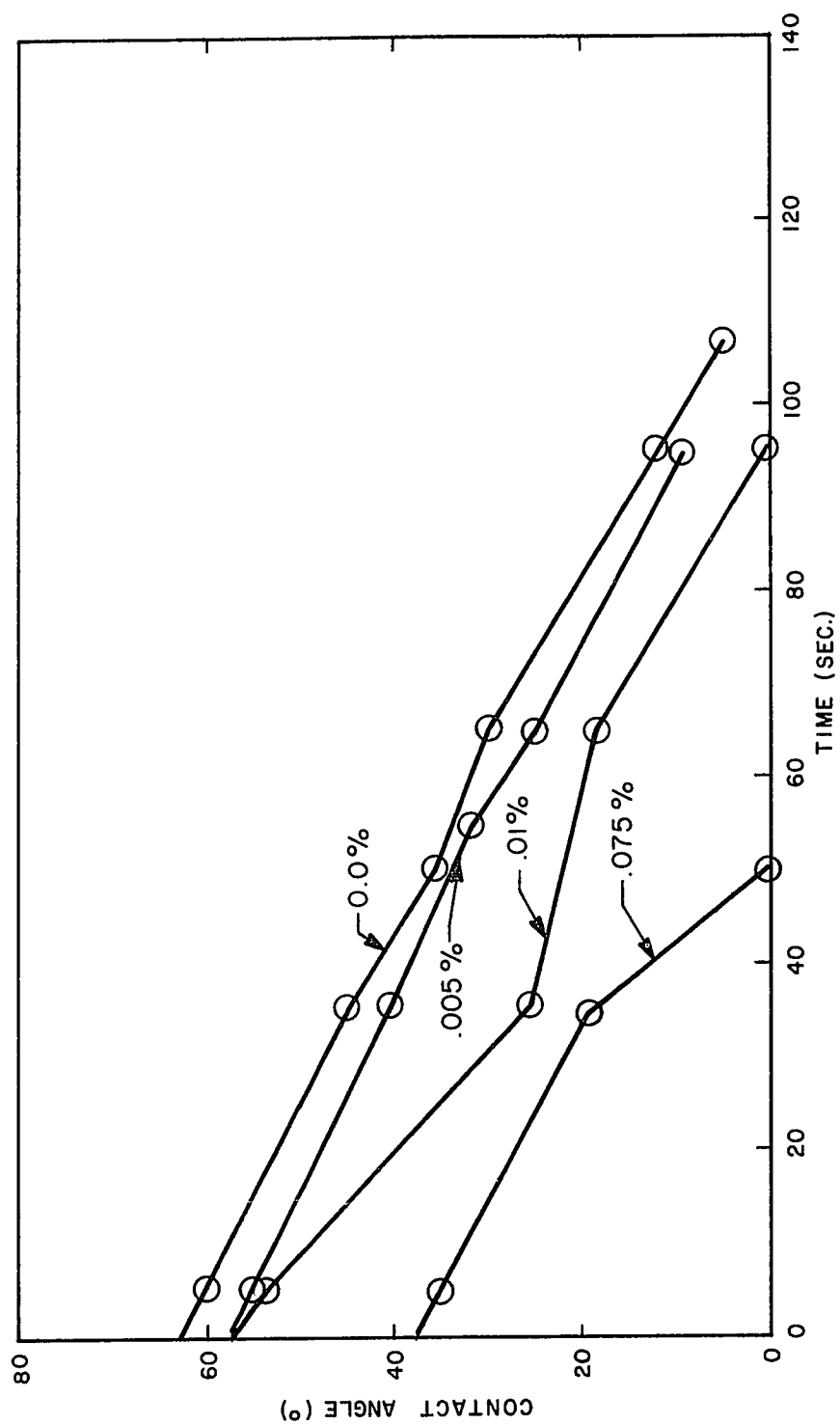


FIGURE 17. TRANSIENT CONTACT ANGLES OF 30-LB, BLEACHED, ROSIN SIZED GROUNDWOOD WITH QUATERNARY AMMONIA SURFACTANT

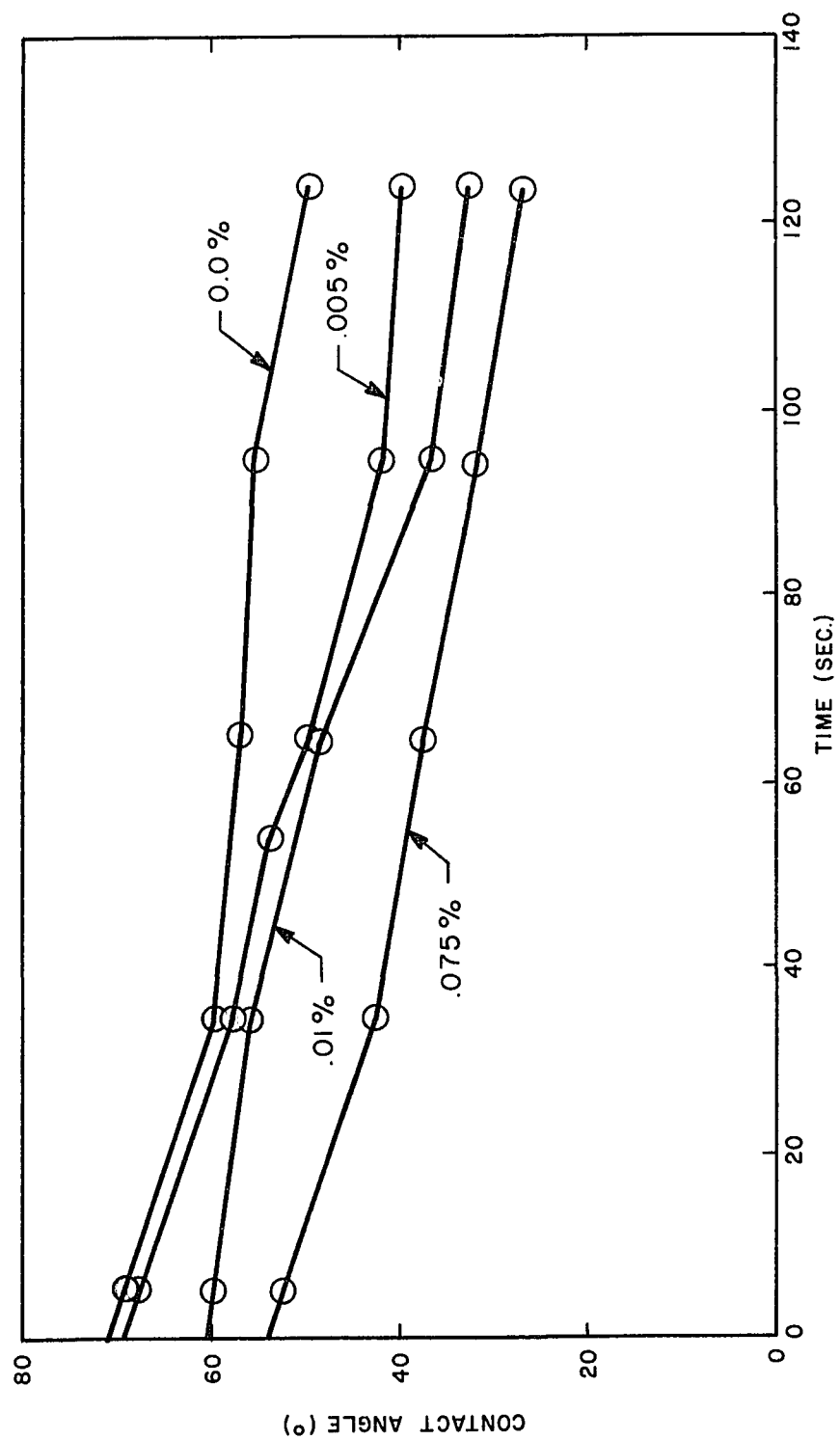


FIGURE 18. TRANSIENT CONTACT ANGLES OF 38-LB, BLEACHED, STARCH SIZED, CLAY COATED GROUNDWOOD WITH QUATERNARY AMMONIA SURFACTANT

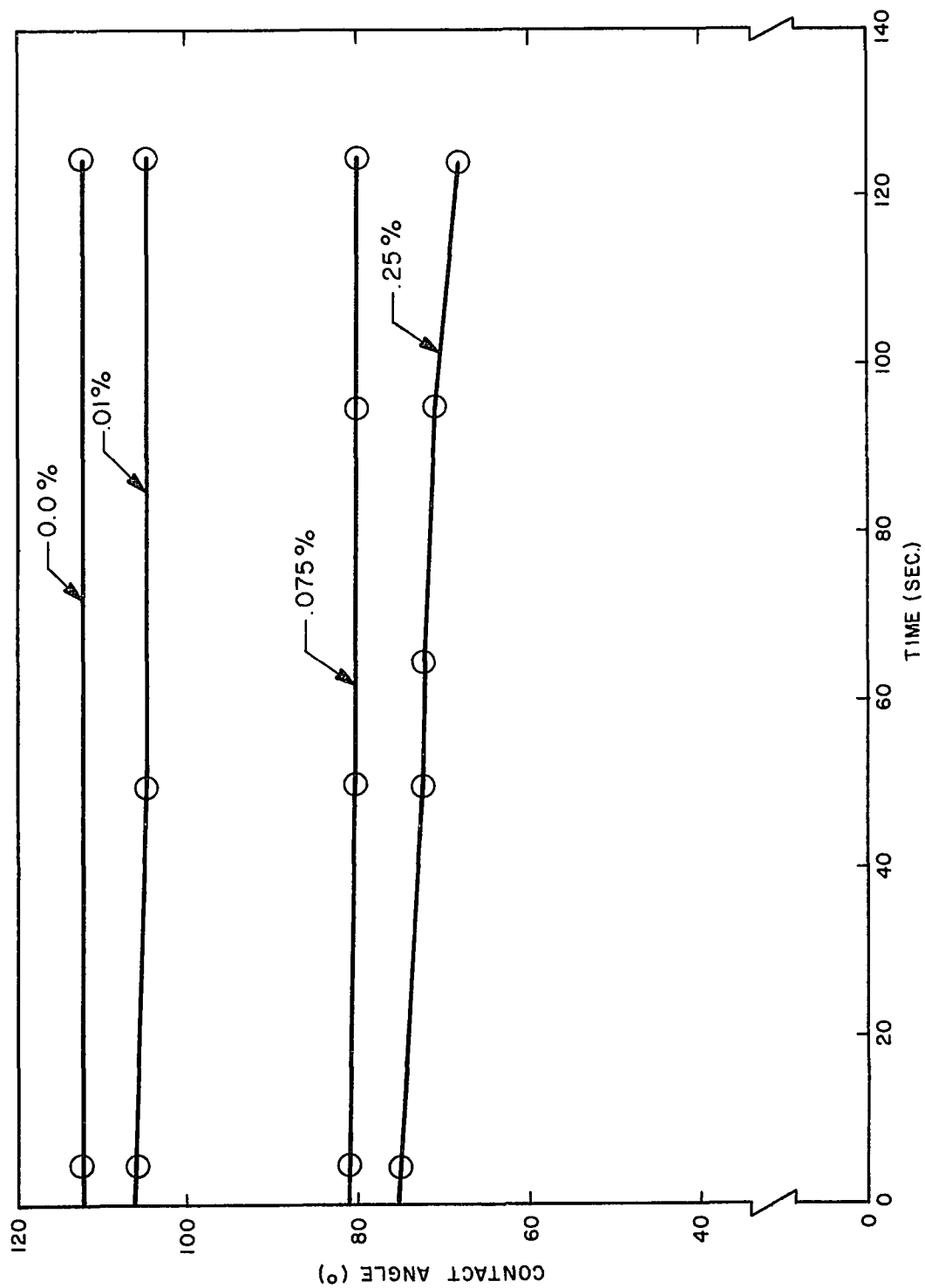


FIGURE 19. TRANSIENT CONTACT ANGLES OF 50-LB, BLEACHED, KRAFT SHIPPING SACK WITH QUATERNARY AMMONIA SURFACTANT

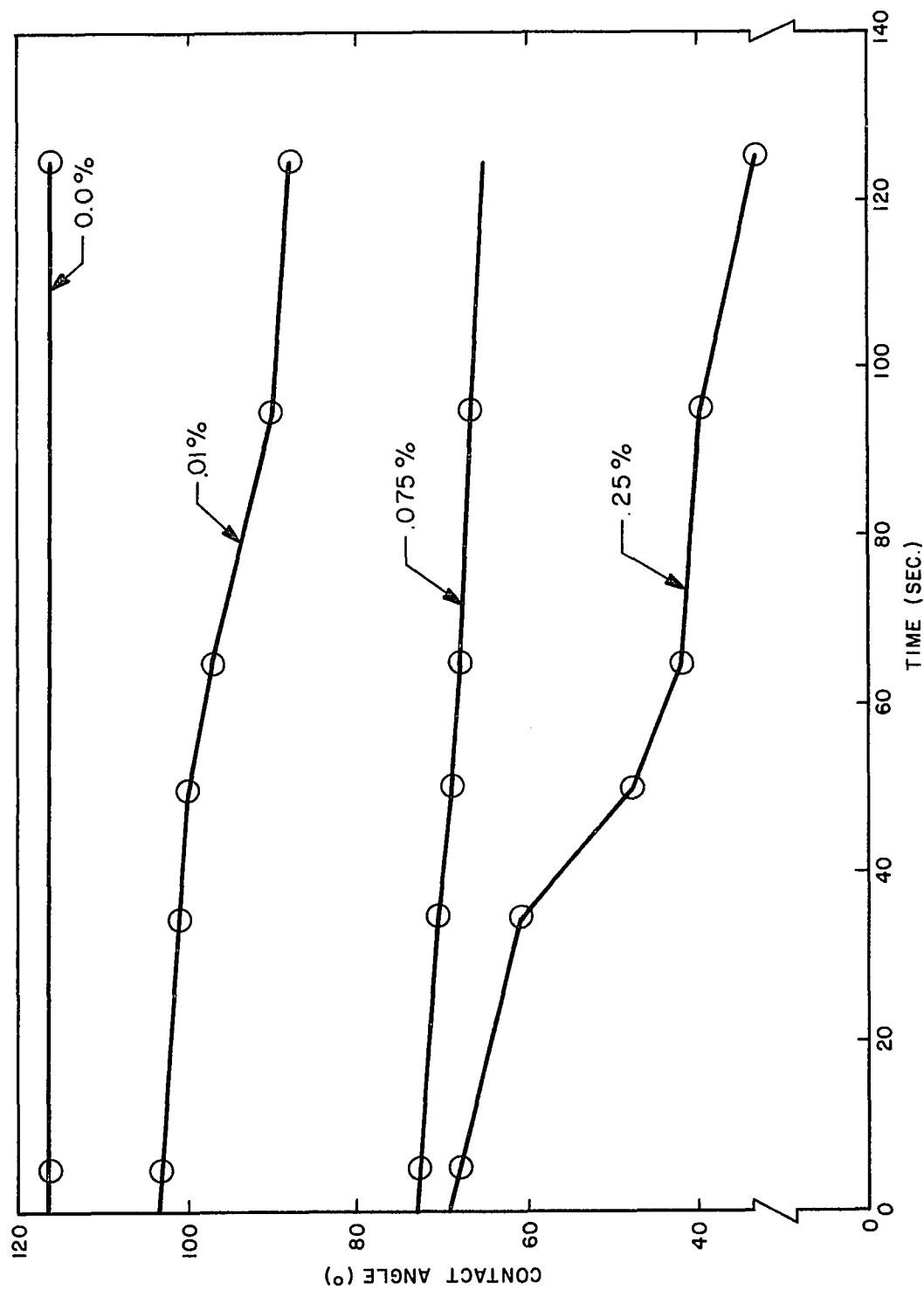


FIGURE 20. TRANSIENT CONTACT ANGLES OF 50-LB, BLEACHED, WET-STRENGTH, KRAFT SHIPPING SACK WITH QUATERNARY AMMONIA SURFACTANT

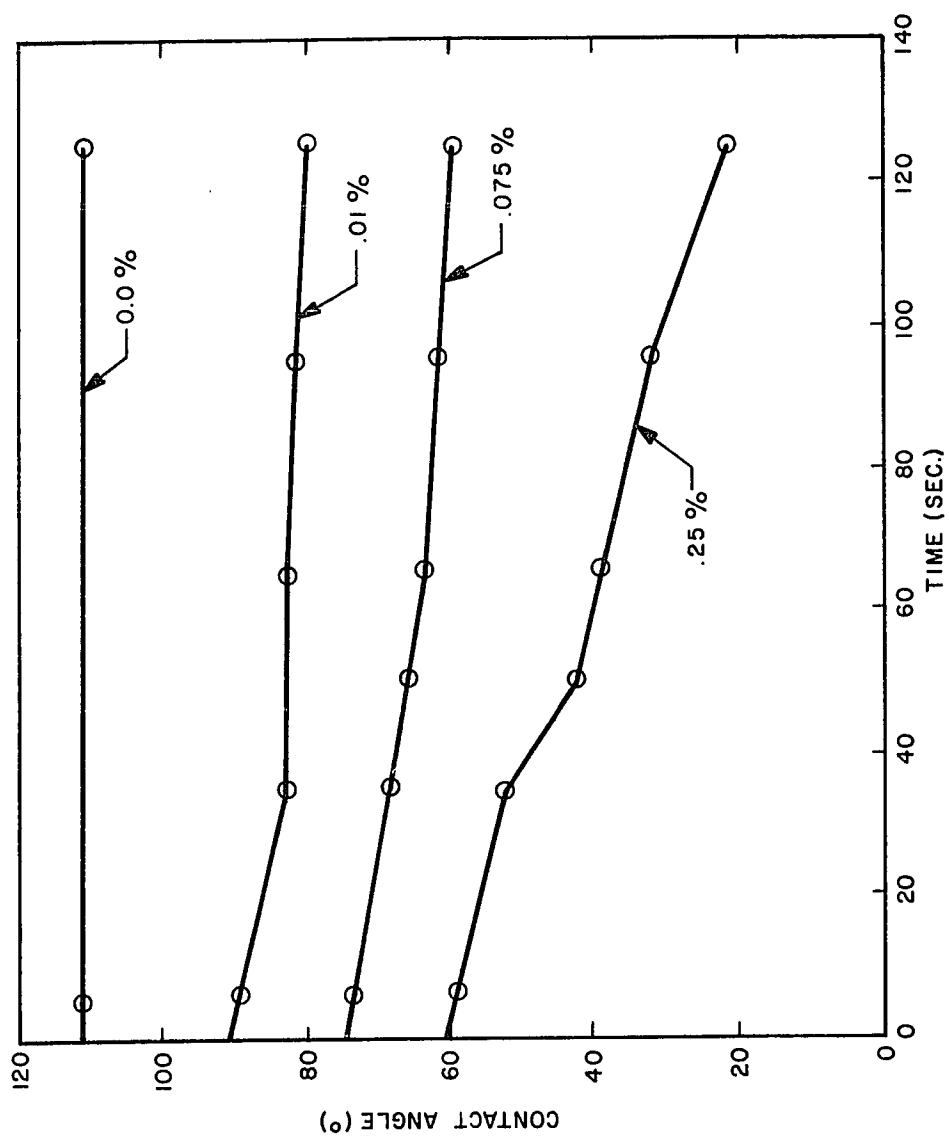


FIGURE 21. TRANSIENT CONTACT ANGLES OF 105-LB, BLEACHED, WAX COATED, SIZED FOODBOARD WITH QUATERNARY AMMONIA SURFACTANT

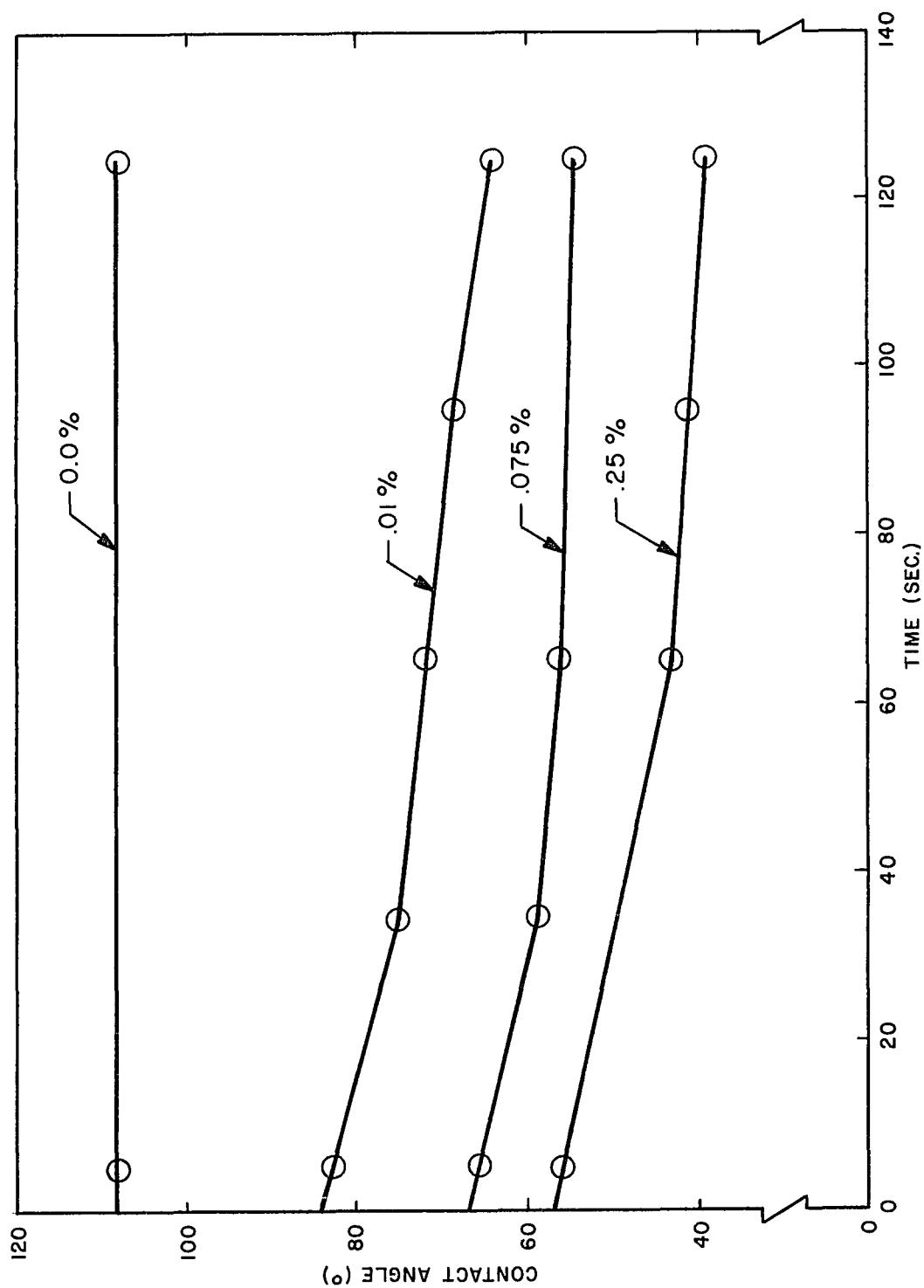


FIGURE 22. TRANSIENT CONTACT ANGLES OF 40-LB, UNBLEACHED, KRAFT SHIPPING SACK WITH QUATERNARY AMMONIA SURFACTANT

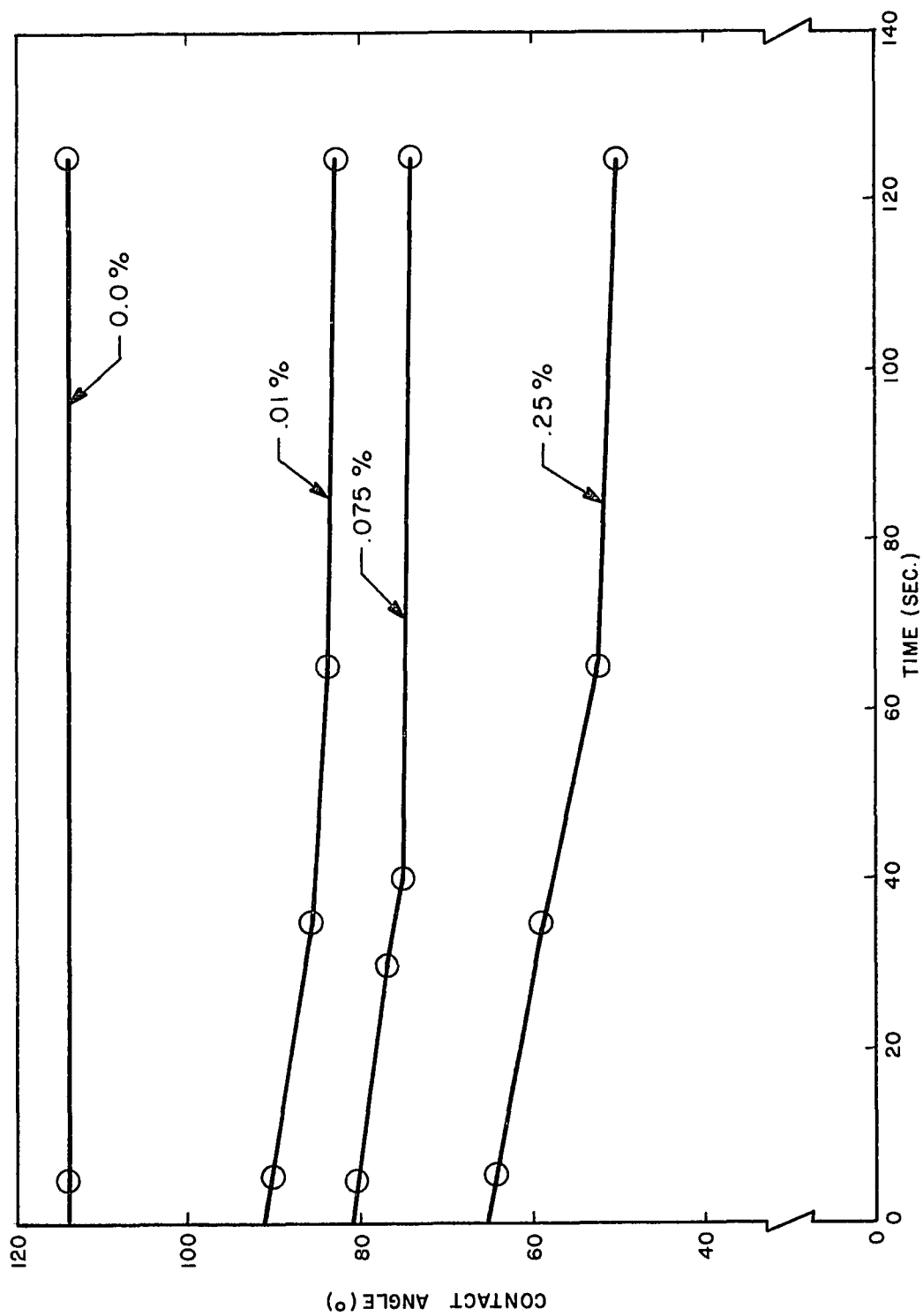


FIGURE 23. TRANSIENT CONTACT ANGLES OF 50-LB, UNBLEACHED, WET-STRENGTH, KRAFT SHIPPING SACK WITH QUATERNARY AMMONIA SURFACTANT



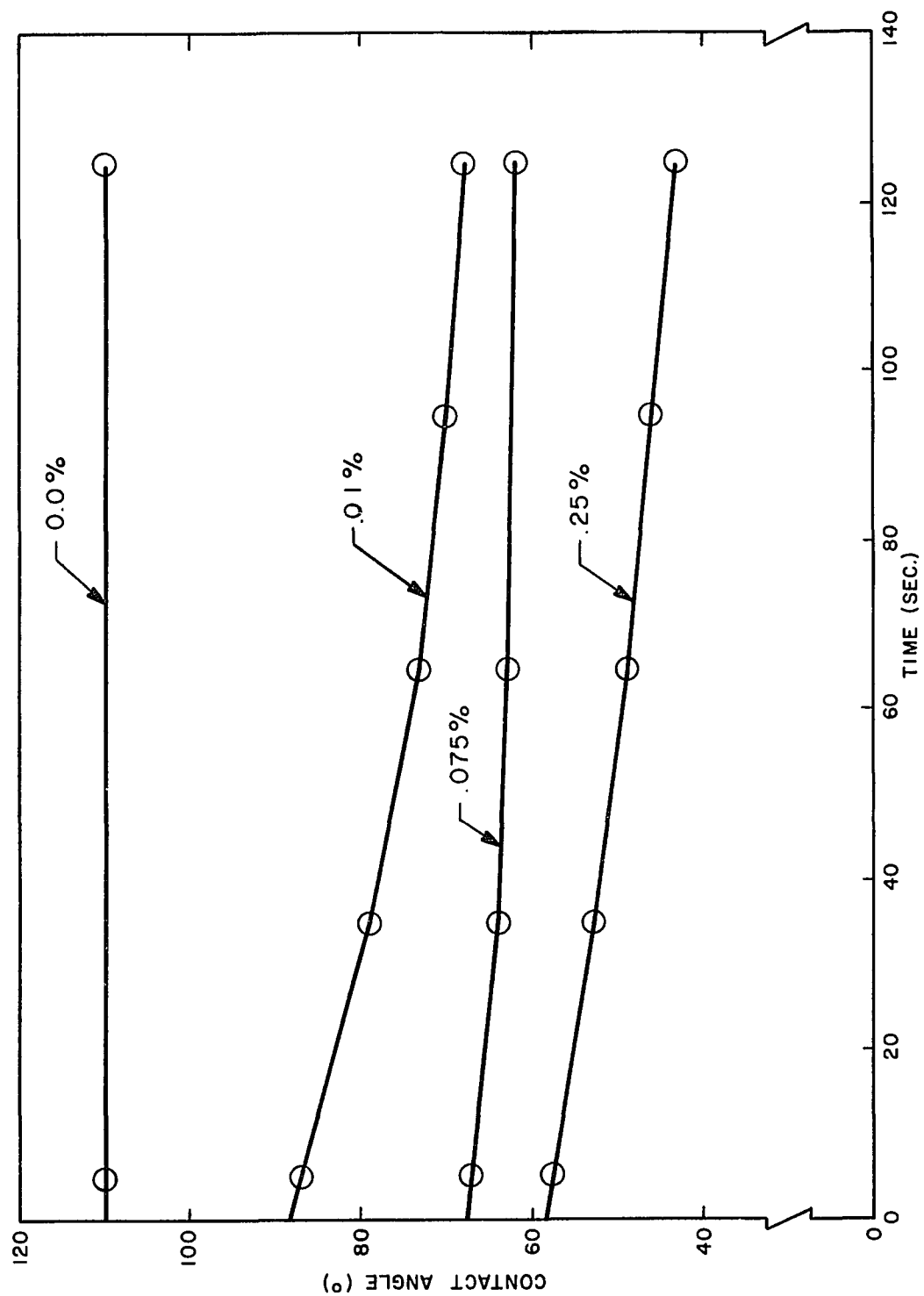


FIGURE 24. TRANSIENT CONTACT ANGLES OF 60-LB, UNBLEACHED, KRAFT SHIPPING SACK WITH QUATERNARY AMMONIA SURFACTANT

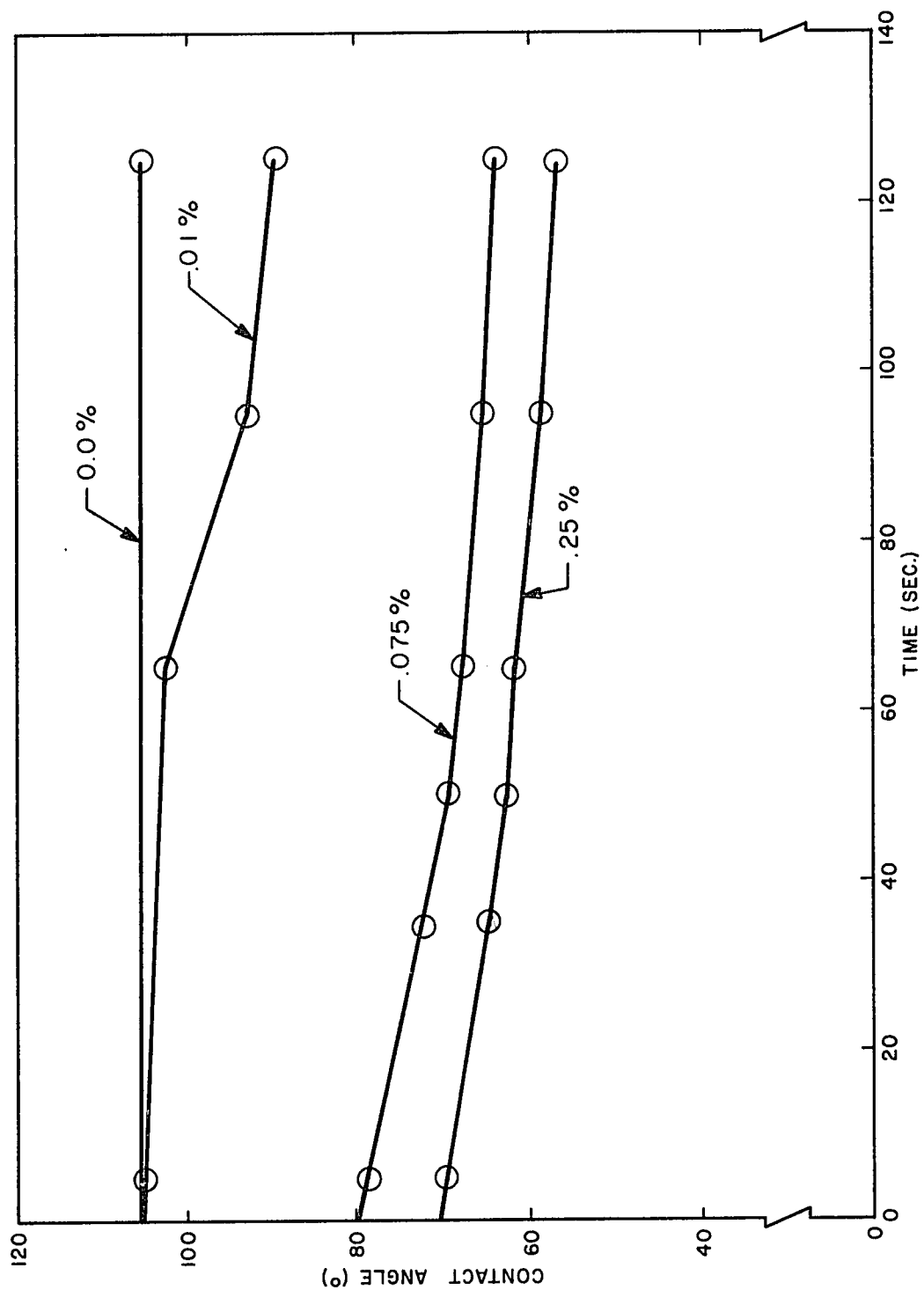


FIGURE 25. TRANSIENT CONTACT ANGLES OF 75-G/M<sup>2</sup>, BLEACHED, SIZED BOND WITH QUATERNARY AMMONIA SURFACTANT

a thickness of .127 mm, exhibited only a slight change of the contact angle for water over the 120 second observation time, from 114 to 106 degrees.

The bleached kraft sack without any additives, had a weight of 50#, but the corresponding unbleached sack of the same weight had a chemical additive to resist wetting. The bleached sack, compared to the unbleached sample is slightly lighter, 50 versus 60#, and thinner, .152 versus .178 mm, but of similar apparent densities, .560 versus .564 g/cm<sup>2</sup> both can be used to determine wetting differences. The relatively stable wetting curves for the bleached kraft samples, from Figure 19, are all appreciably higher than those for the unbleached sack, Figure 24.

The wetting curves for the two bleached sulfite papers are shown on Figures 21 and 25. These papers possess quite dissimilar physical and chemical properties. The 105#(170.88 g/m<sup>2</sup>) foodboard container was wax coated and double walled with a sheet thickness of .285 mm; the bond had a unit weight of 75 g/m<sup>2</sup> and a sheet thickness of .114 mm, and was uncoated.

Figures 19 and 20 show the results obtained for bleached kraft papers having identical basis weights of 55#(81.37 g/m<sup>2</sup>), sheet thicknesses of .152 mm, and apparent densities of .558 g/cm<sup>3</sup>. The important parameter that differentiates these samples is the wet-strength additive applied to one of these papers. When water was applied as the wetting agent, the regular-strength kraft paper, Figure 19, shows a constant contact angle of 112.5°. Figure 20 shows a constant contact

angle of  $116^{\circ}$ . The curves in Figure 19 are relatively stable with a change of 1 to 7 degrees over the 2 minute observation period. Figure 20 shows that the curves of the wet-strength kraft sample, while lower initially, exhibit significant changes, dropping 8 to 26 degrees, during this same time .

The surface wetting behaviors of the unbleached kraft shipping sacks are shown on Figures 22 to 24. There are two major variables associated with these papers. First, the basis weights for these samples included 40#(65.10 g/m<sup>2</sup>), 50#(81.37 g/m<sup>2</sup>), and 60#(97.65 g/m<sup>2</sup>). Also, the 50# sack had been subjected to a wet-strength additive.

#### Anionic Surfactant

The transient contact angles obtained for water and various concentrations of the anionic surfactant on several paper samples are shown on Figures 26 to 30. These transient contact angles shown were also extended past the 5 sec time interval to establish the initial values. The behavior of the anionic surfactant showed similarities on many of the papers with those obtained with the cationic species.

Figures 26 and 27 show the behavior of the anionic surfactant on the bleached kraft shipping sacks. These papers were identical in all respects except for the wet-strength additive applied to one of the samples. The curves for this sample are lower than those for the paper without the additive when the anionic surfactant is used.

The surface wetting behaviors of the unbleached kraft shipping sacks are shown in Figures 28 to 30. The data points shown, as well as those used throughout this work, in general represent averages taken between 6 and 10 observations.

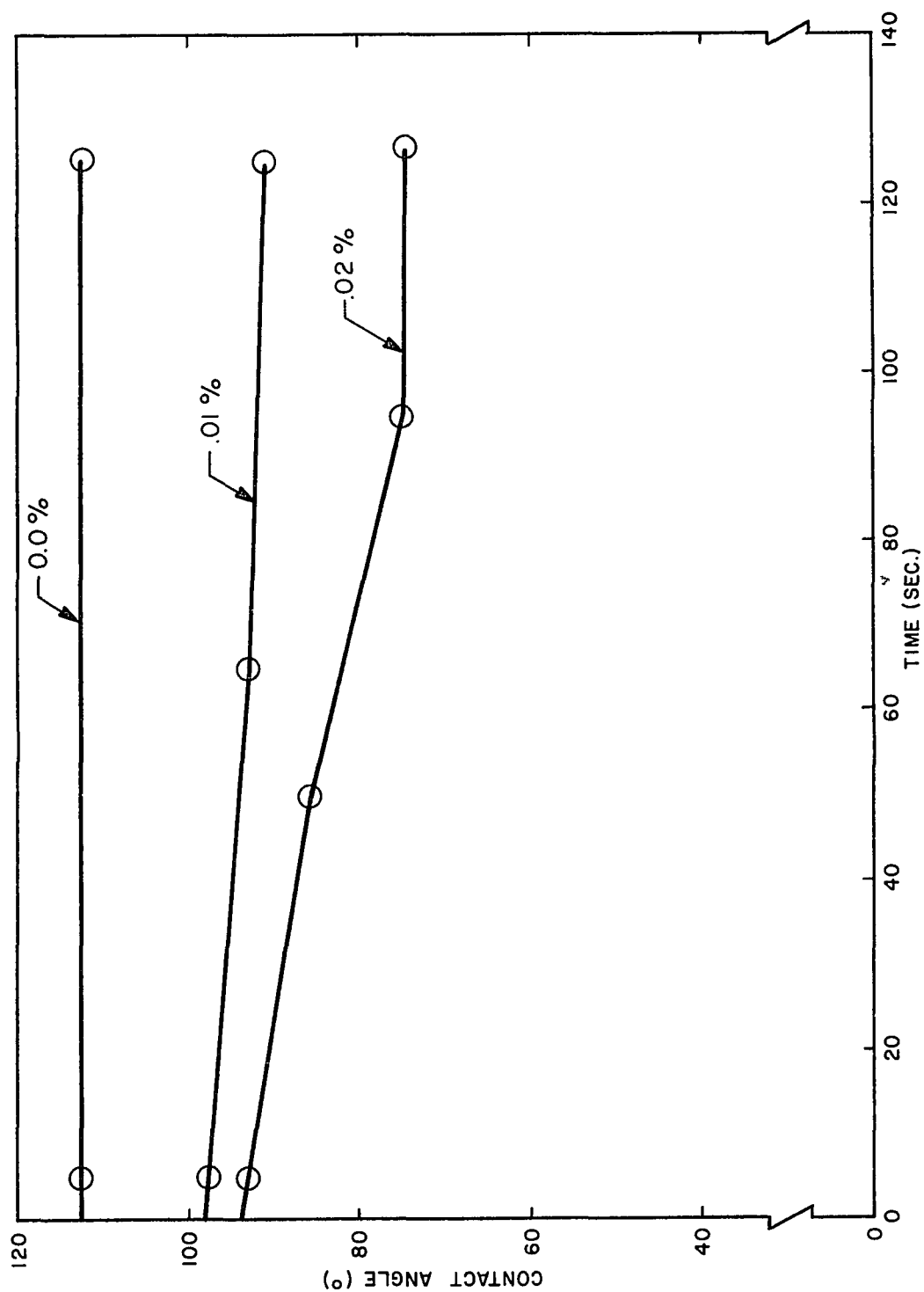


FIGURE 26. TRANSIENT CONTACT ANGLES OF 50-LB, BLEACHED, KRAFT SHIPPING SACK WITH ALKYL ARYL SULFONATE

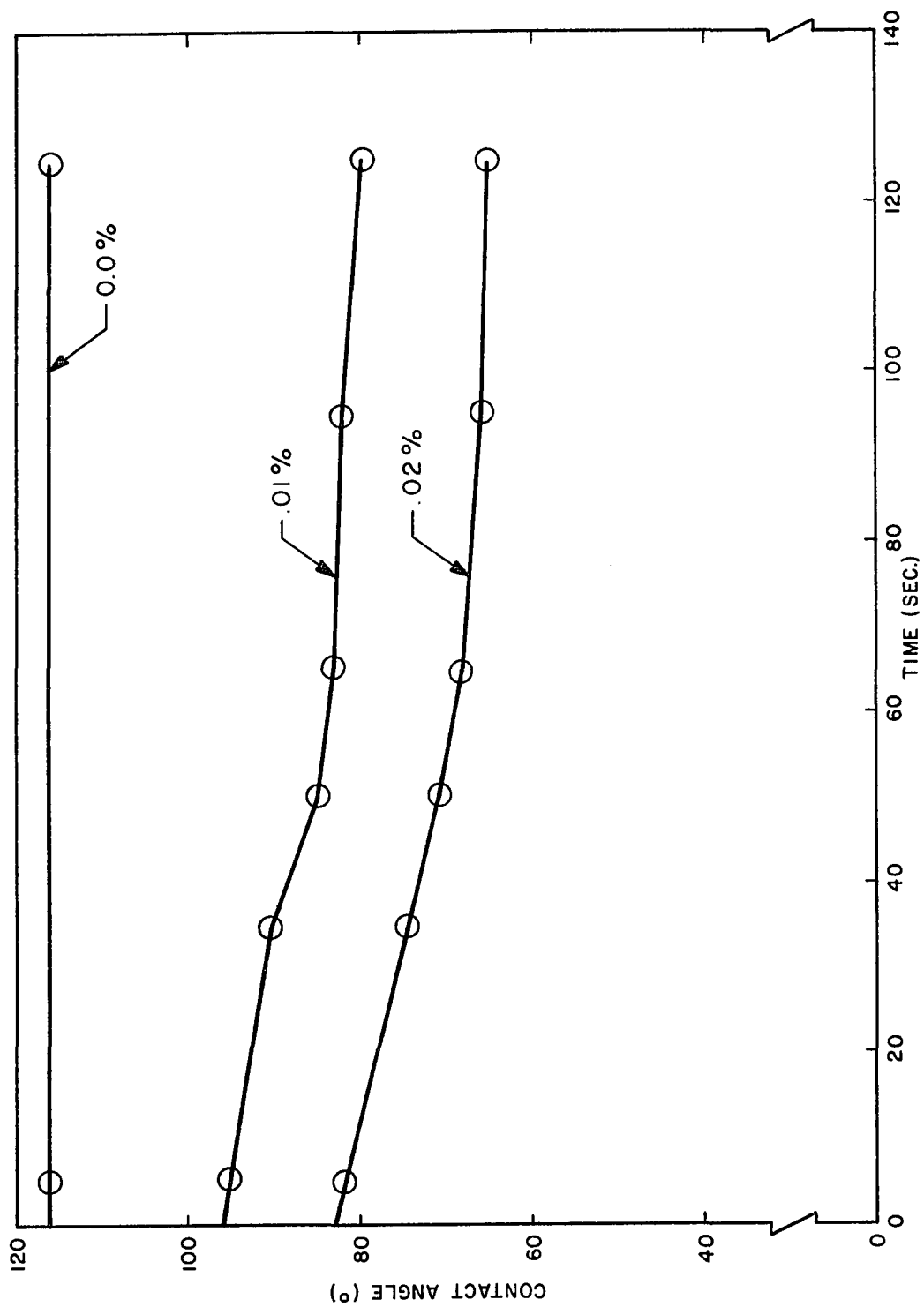


FIGURE 27. TRANSIENT CONTACT ANGLES OF 50-LB, BLEACHED, WET-STRENGTH, KRAFT SHIPPING SACK WITH ALKYL ARYL SULFONATE

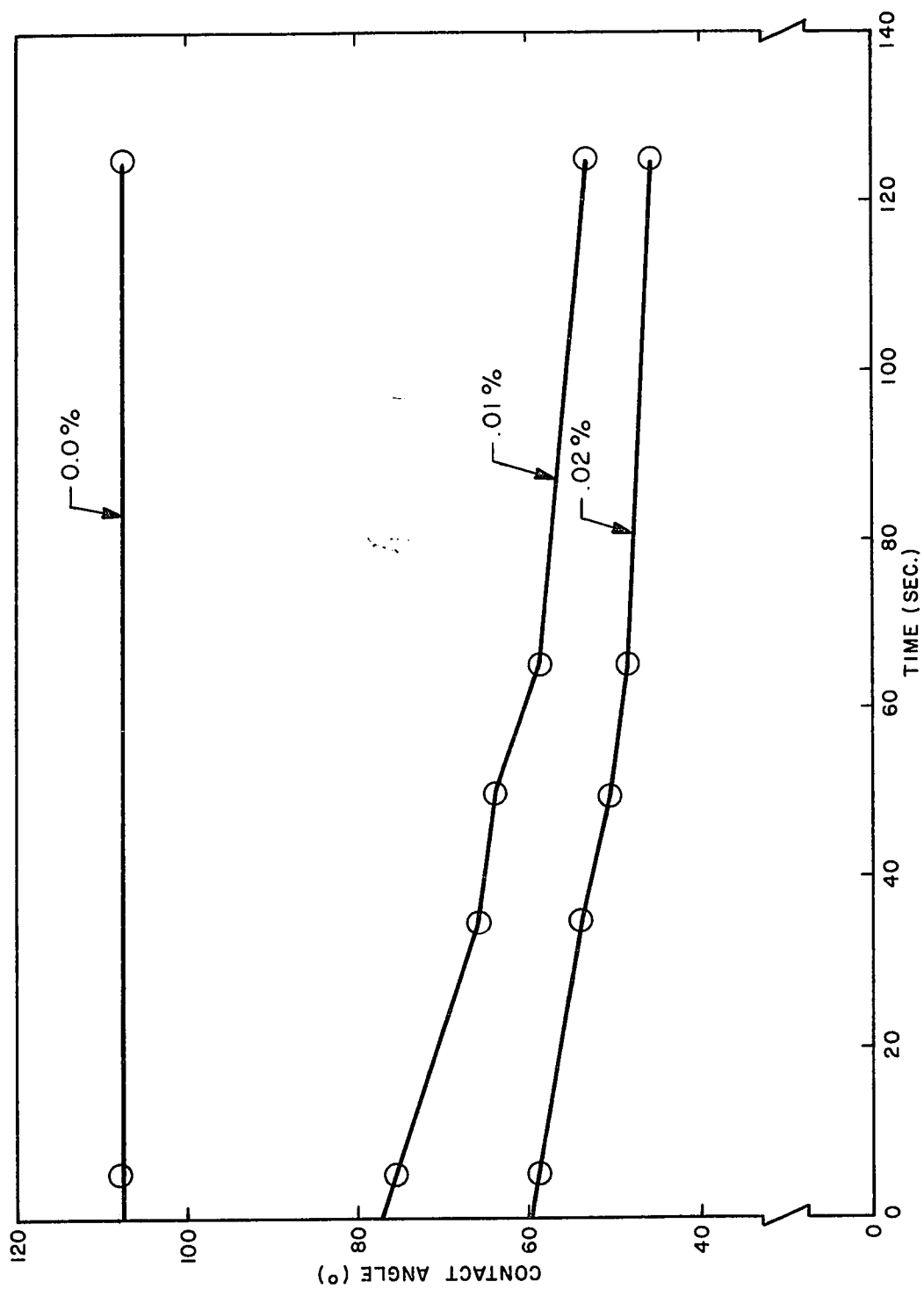


FIGURE 28. TRANSIENT CONTACT ANGLES OF 40-LB, UNBLEACHED, KRAFT SHIPPING SACK WITH ALKYL ARYL SULFONATE

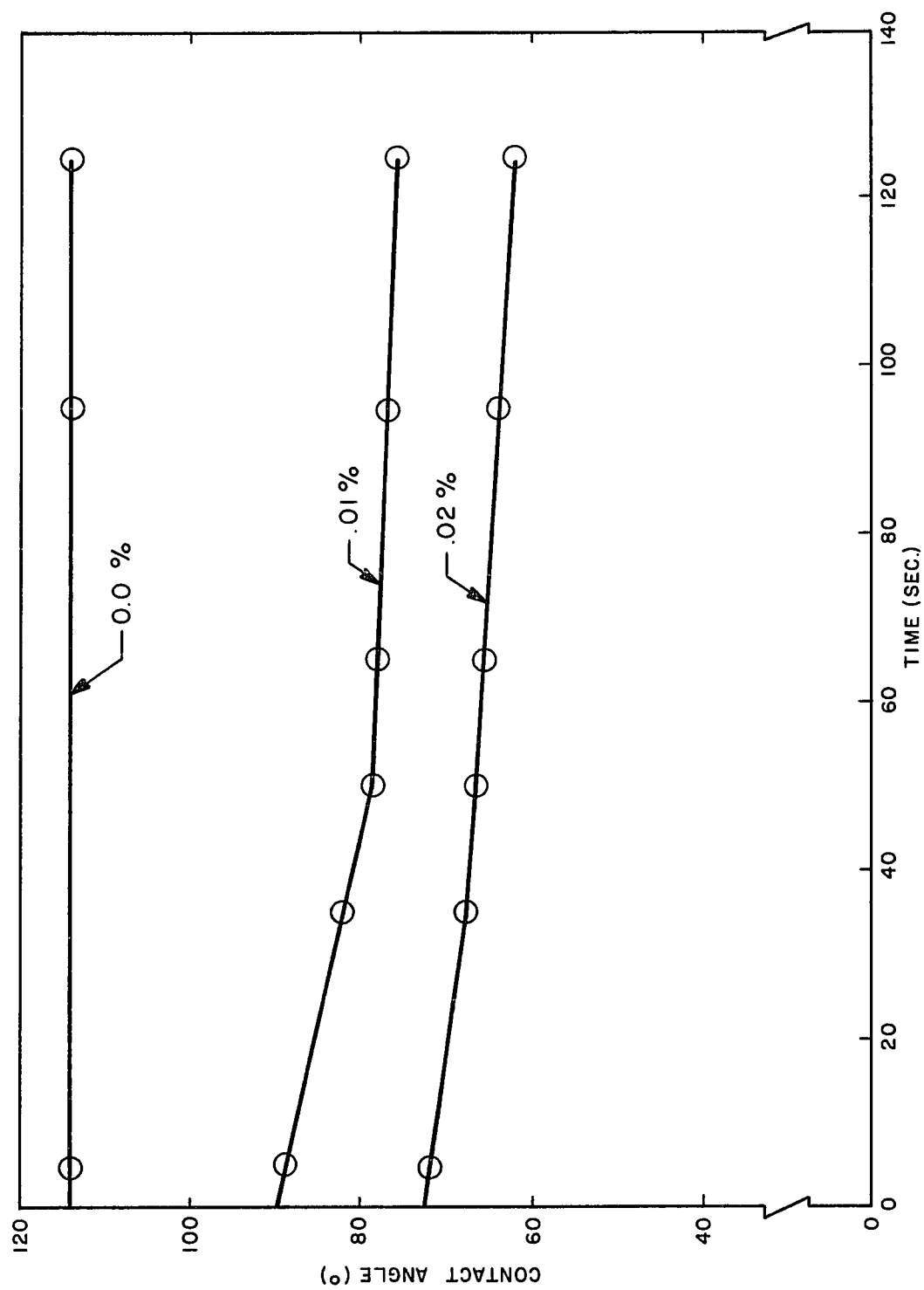


FIGURE 29. TRANSIENT CONTACT ANGLES OF 50-LB, UNBLEACHED, WET-STRENGTH, KRAFT SHIPPING SACK WITH ALKYL ARYL SULFONATE



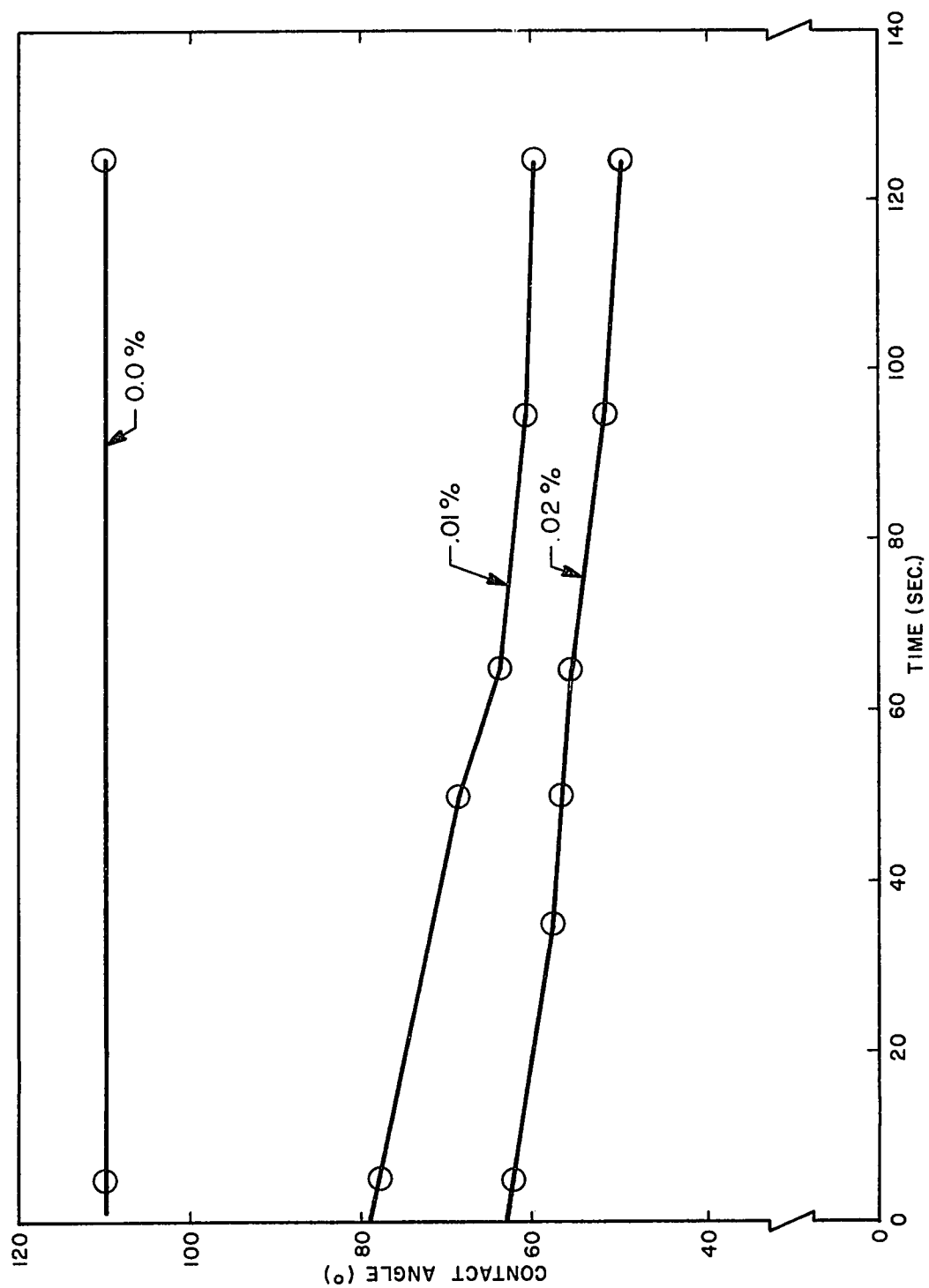


FIGURE 30. TRANSIENT CONTACT ANGLES OF 60-LB, UNBLEACHED, KRAFT SHIPPING SACK WITH ALKYL ARYL SULFONATE

### CAPILLARY PENETRATIONS

Capillary penetrations were recorded for pure water and various concentrations of a cationic and an anionic surfactant on all of the paper samples. The concentrations, 0.01, 0.1, 0.25, 0.50, 0.75, and 1.0 percent, were all derived by diluting the surfactants with deionized water. Because of the low concentrations, the viscosities of all liquids were assumed to be close to that of water. The cationic surfactant tested was a quaternary ammonium derivative (Atlas G-3634A); the anionic was an alkyl aryl sulfonate (Atlas G-3300).

While all paper samples were subjected to water and all of the various concentrations of the wetting agents, capillary penetration did not occur in all the strips under all wetting conditions. Because of the variety of papers studied, the results are quite different and will be discussed under subsections dealing with the capillary wetting of groundwoods, papers penetrated by the cationic surfactant, and those wetted by the anionic surfactant.

#### Capillary Wetting of Groundwoods

The only group of papers that was wetted by water and all the various concentrations of the surfactants was the bleached groundwood papers. The penetration was appreciable for the catalog and textweb and less pronounced for the offset book paper. These, also, were the only papers under which capillary wetting occurred using pure water as the wetting liquid. The non-groundwood papers did not show any capillary wetting when subjected to water for over a 24 hour period.

The results of using water and various concentrations of the cationic surfactant for capillary wetting on the rosin and starch sized groundwoods are shown on Figures 31 and 32, respectively. Figures 33 and 34 show the results of the capillary movement plotted against time for these samples, respectively, while being wetted in water and various anionic surfactant concentrations. In all cases the rate of capillary penetration and the height achieved at any observation time using either surfactant is less than that obtained when pure water was used as the wetting liquid. For instance, catalog paper showed a capillary penetration of 57 mm in one hour for pure water and a rise between 40 and 46 mm for this same time when the cationic surfactant was used as the wetting agent, Figure 31. The various concentrations of the anionic detergent resulted in capillary penetrations varying between 38 and 52 mm over this 60 minute period, Figure 33. Similarly the depth of penetration for the textweb groundwood in water for 60 minutes was 34 mm. The range of penetration for the cationic surfactant over this period, was 20 to 24 mm, Figure 32; the anionic resulted in depths from 18 to 25 mm, as shown in Figure 34.

A summary of the capillary wetting rates of the catalog groundwood for the various liquids is compiled in Table 24. The wetting liquids and various concentrations of the surfactants are shown in the first column. The second column shows the observed rate of capillary penetration, in mm/hr. This data is compared with the theoretical capillary wetting power,  $\gamma_{LG} \cos \theta$ , shown in the next column. This product is a result obtained from previous determinations of the surface tensions and initial contact angles for the various wetting liquids.

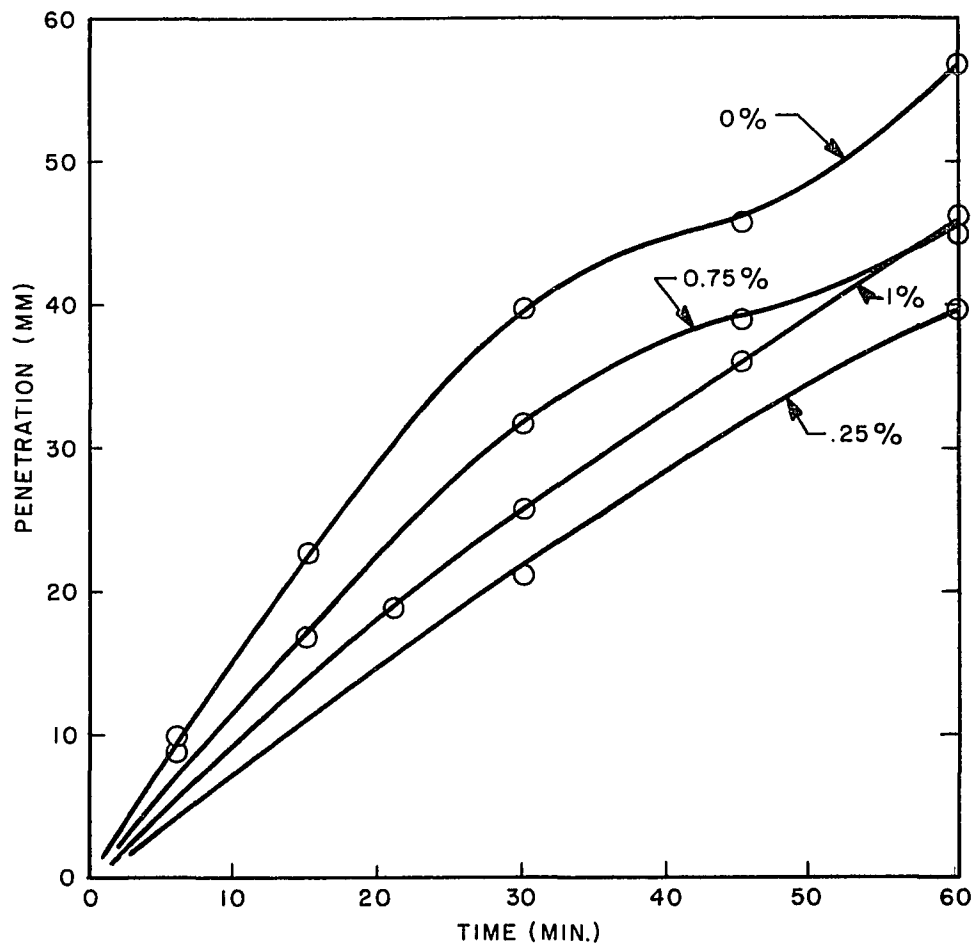


FIGURE 31. CAPILLARY PENETRATION INTO 30-LB, BLEACHED, ROSIN SIZED GROUNDWOOD WITH QUATERNARY AMMONIA SURFACTANT

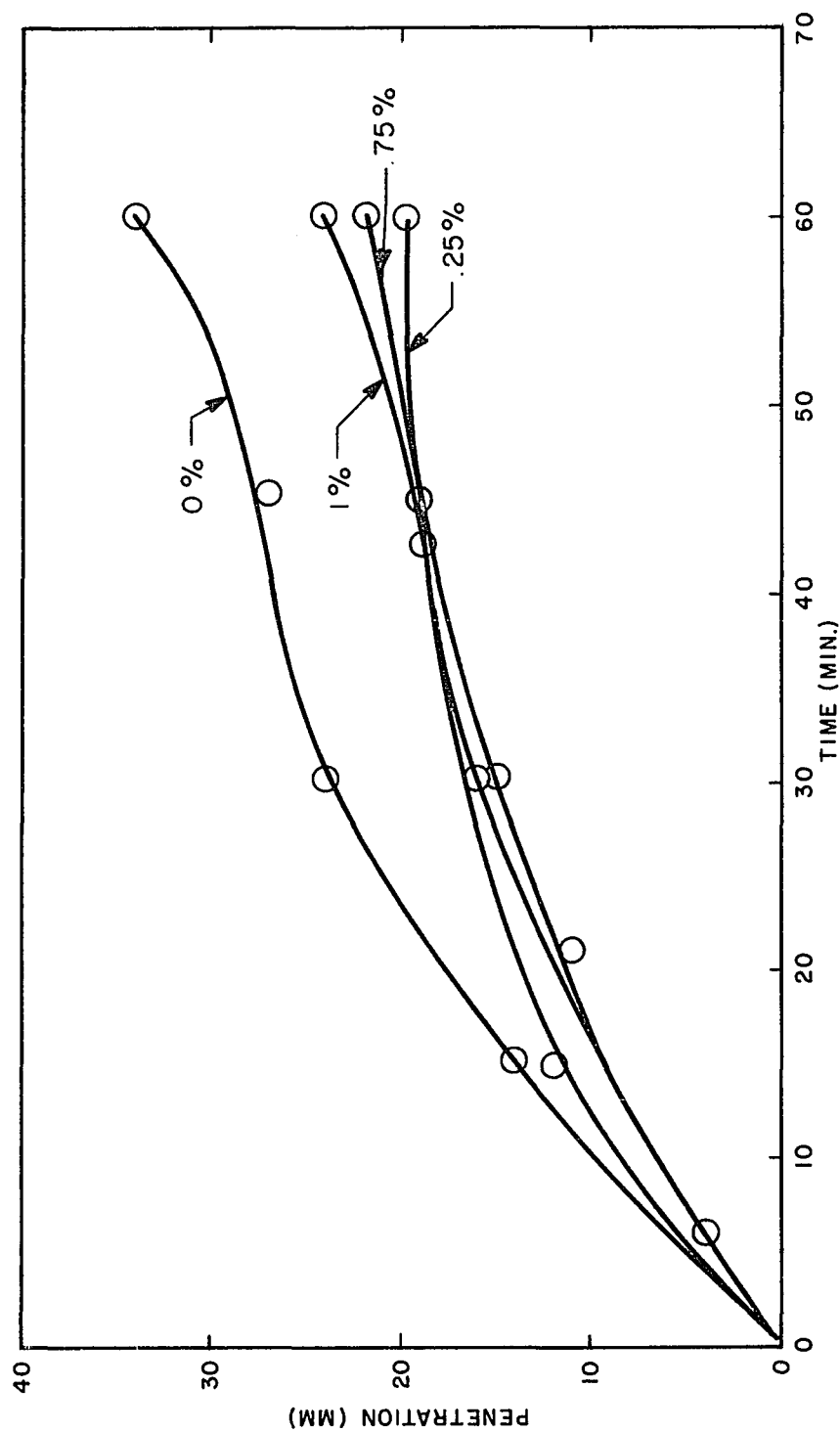


FIGURE 32. CAPILLARY PENETRATION INTO 38-LB, BLEACHED, STARCH SIZED, CLAY COATED GROUNDWOOD WITH QUATERNARY AMMONIA SURFACTANT

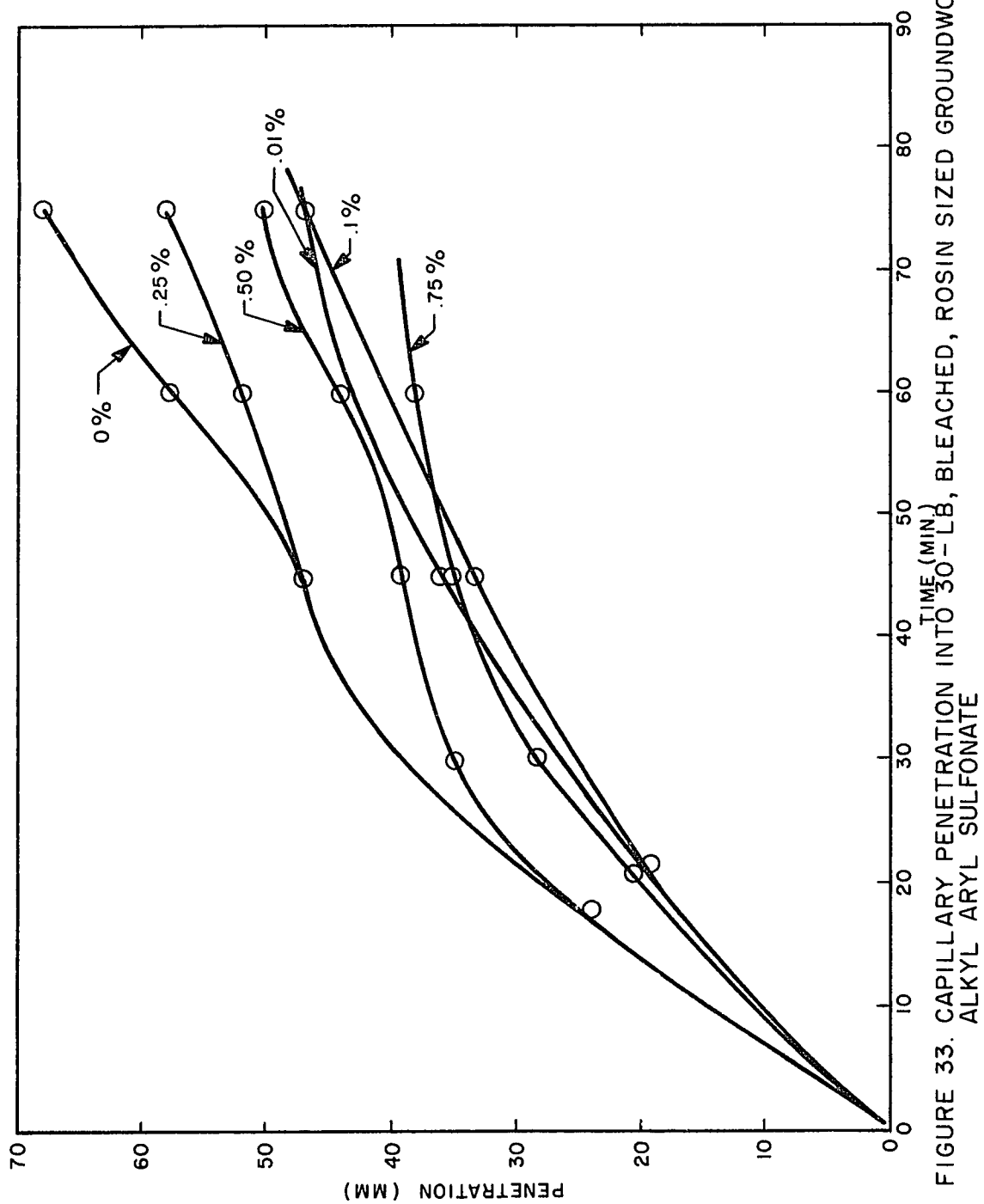


FIGURE 33. CAPILLARY PENETRATION INTO 30-LB, BLEACHED, ROSIN SIZED GROUNDWOOD WITH ALKYL ARYL SULFONATE

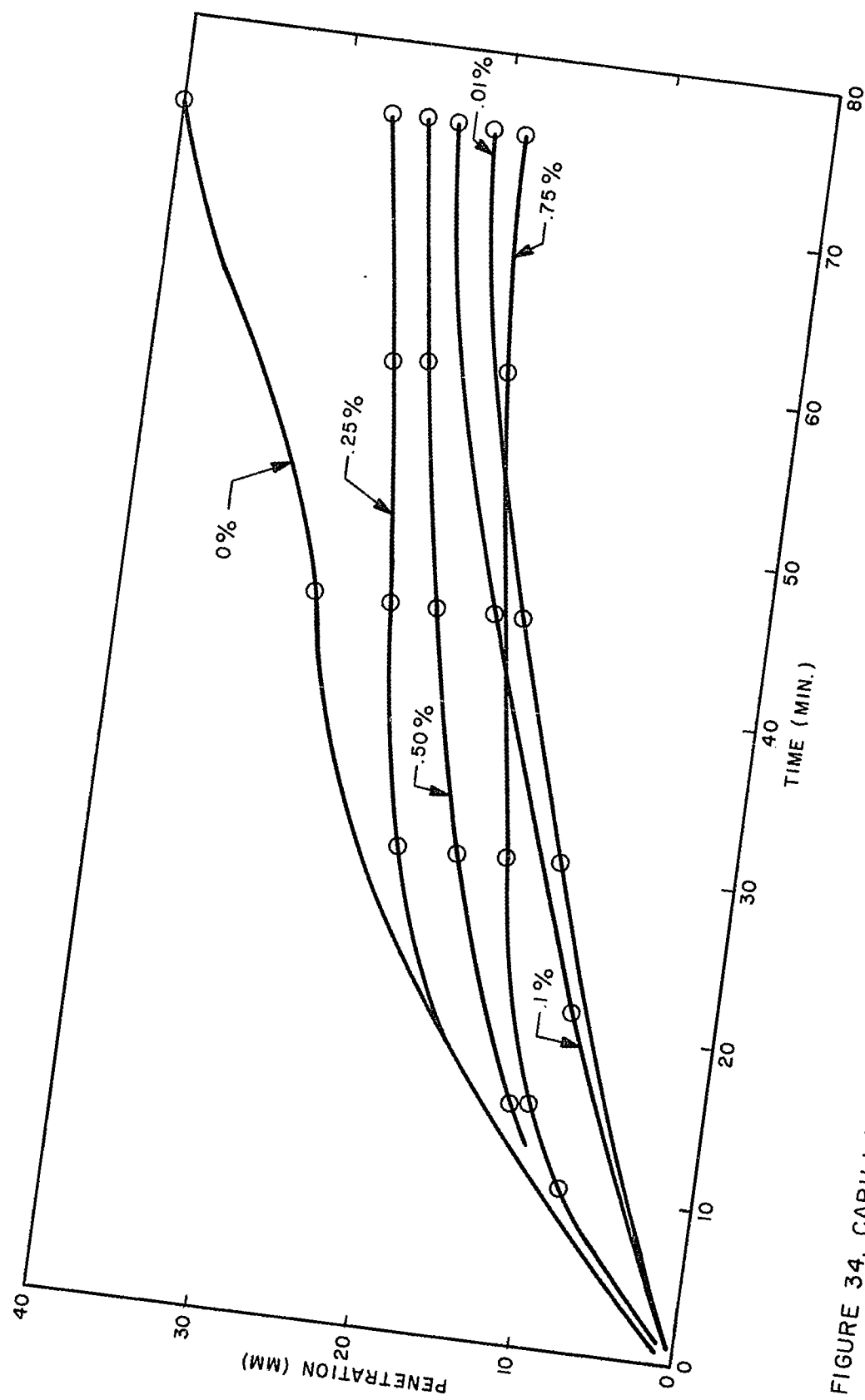


FIGURE 34. CAPILLARY PENETRATION INTO 38-LB, BLEACHED, STRACH SIZED, CLAY COATED  
GROUNDWOOD WITH ALKYL ARYL SULFONATE

| (1)<br>WETTING<br>LIQUID | (2)<br>RATE OF CAPILLARY<br>MOVEMENT,<br>(mm/hr) | (3)<br>CAPILLARY WETTING<br>POWER,<br>$\gamma_L \cos \theta$ | (4)<br>K= (2) $\frac{1}{r}$ (3) |
|--------------------------|--|--|---------------------------------|
| Water                    | 57   | 33.6   | 1.69                            |
| Cationic (G-3634A)       |  |  |                                 |
| 0.25%                    | 40   | 36.0   | 1.11                            |
| 0.75%                    | 45   | 37.0   | 1.22                            |
| 1.00%                    | 46   | 38.0   | 1.21                            |
| Anionic (G-3300)         |  |  |                                 |
| 0.01%                    | 43   | 23.5   | 1.83                            |
| 0.10%                    | 40   | 28.1   | 1.42                            |
| 0.25%                    | 52   | 29.0   | 1.79                            |
| 0.50%                    | 44   | 29.5   | 1.49                            |
| 0.75%                    | 36   | 30.0   | 1.20                            |

TABLE 24. SUMMARY OF CAPILLARY WETTING OF GROUNDWOOD CATALOG PAPER BY WATER AND VARIOUS SURFACTANT CONCENTRATIONS



If the capillary system of the paper is constant without any chemical interferences, a proportionality factor should be constant for all the tested liquids. This factor, K, is shown in the last column and was determined from the Lucas-Washburn equation:<sup>(55)</sup>

$$\text{rate of capillary movement (mm/hr)} = K \gamma_{LG} \cdot \cos \theta$$

or

$$K = \frac{\text{rate of capillary movement}}{\text{capillary wetting power}}$$

Table 25, summarized for the internally rosin sized textweb with a clay coating, shows that the proportionality factors for both surfactants are appreciably lower than that obtained for water.

The results shown in Tables 24 and 25 show that the rates fall into two groups, depending upon the choice of wetting liquid. The proportionality factors within these groups are fairly constant.

#### Non-groundwoods and Cationic Surfactant

When the various concentrations of the quaternary ammonium derivative cationic surfactant were used to capillary wet the papers, it was found that several other non-groundwood sample grades showed penetration and other grades resisted this form of wetting. For this range of concentrations, capillary penetration occurred in all bleached papers. These include the groundwoods, sulfites, and the kraft shipping sacks. The group of papers that did not demonstrate this form of wetting consisted of all the different weight unbleached kraft shipping sacks.

Figure 35 shows the depth of penetration for the bleached kraft sacks over a 75 minute period when they were wetted with the 0.75% cationic surfactant concentration. The slope of the penetration

| (1)<br>WETTING<br>LIQUID | (2)<br>RATE OF CAPILLARY<br>MOVEMENT,<br>(mm/hr) | (3)<br>CAPILLARY WETTING<br>POWER,<br>$\gamma_{LG} \cdot \cos \theta$ | (4)<br>$K = (2) \div (3)$ |
|--------------------------|--|---|---------------------------|
| Water                    | 34   | 23.7  | 1.42                      |
| Cationic (G-3634A)       |  |   |                           |
| 0.25%                    | 20   | 36.0  | 0.56                      |
| 0.75%                    | 22   | 37.0  | 0.59                      |
| 1.00%                    | 24   | 38.0  | 0.63                      |
| Anionic (G-3300)         |  |   |                           |
| 0.01%                    | 19   | 19.4  | 0.98                      |
| 0.10%                    | 20.5   | 28.1  | 0.73                      |
| 0.25%                    | 25   | 29.0  | 0.86                      |
| 0.50%                    | 23   | 29.5  | 0.78                      |
| 0.75%                    | 18   | 30.0  | 0.60                      |

TABLE 25. SUMMARY OF CAPILLARY WETTING OF GROUNDWOOD TEXTWEB PAPER BY WATER AND VARIOUS SURFACTANT CONCENTRATIONS

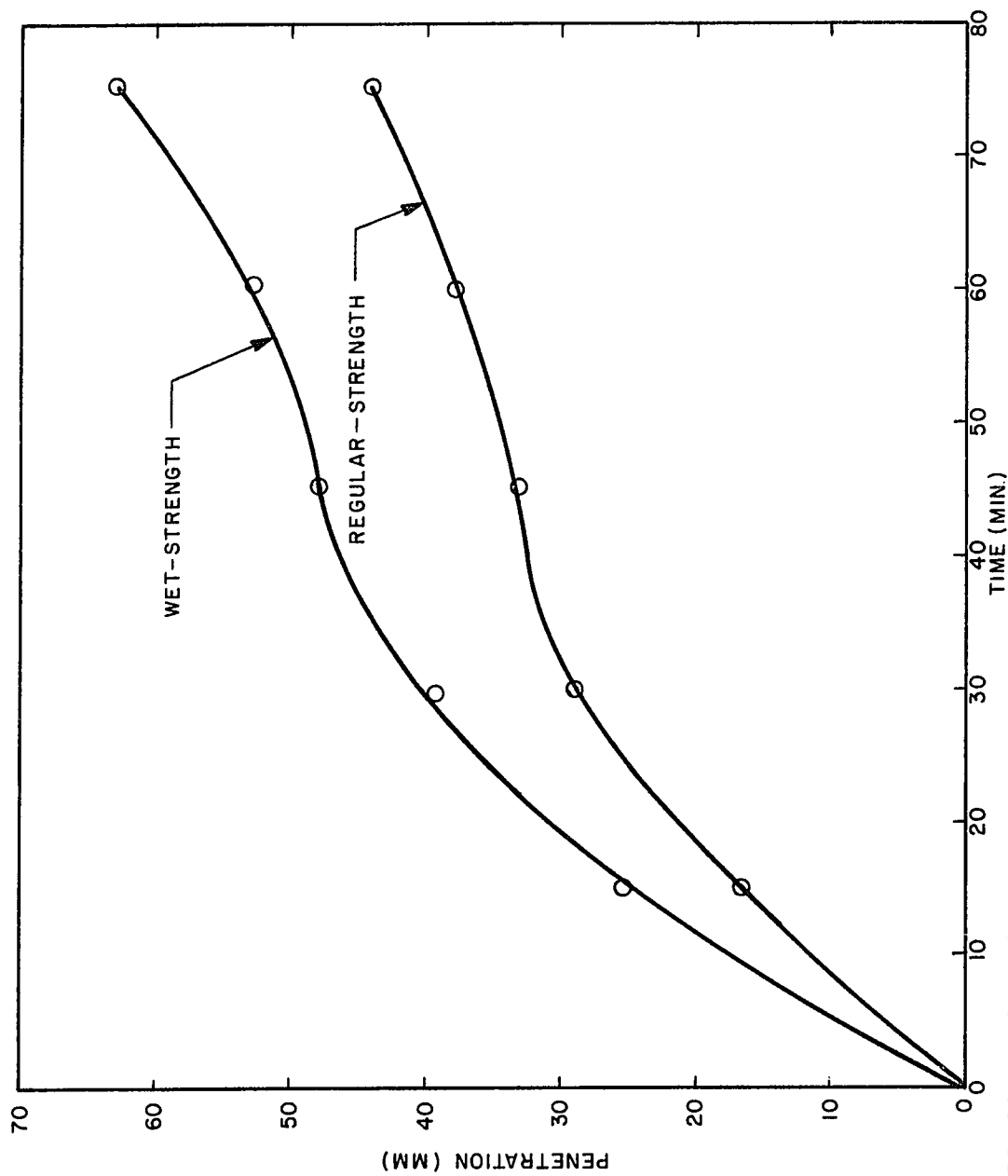


FIGURE 35. CAPILLARY PENETRATION INTO 50-LB, BLEACHED, KRAFT SHIPPING SACKS WITH 0.75% QUATERNARY AMMONIA SURFACTANT

curve and the depth of movement, for any observation time, are always higher for the paper with the wet-strength additive than for the untreated sample. These bleached kraft sacks were identical in all other respects except for this particular additive. The wet-strength additive results in both faster surface wetting and faster capillary wetting than the untreated sample.

#### Non-groundwoods and Anionic Surfactant

When the various concentrations of the alkyl aryl sulfonated anionic surfactant were used to capillary wet the paper samples, it was found that, besides the groundwoods, only the unbleached kraft sacks showed this form of wetting.

Figure 36 shows the capillary penetration over a 30 minute period for the three unbleached kraft papers using a concentration of 0.25% sulfonated surface-active agent. The unbleached papers shown on this figure all have different basis weights and, in addition, one had been treated with a wet-strength additive. The penetration curve for this 50#, wet-strength paper has a different shape from those for the other untreated samples. Its wetting curve begins slower and then accelerates faster than the other two curves.

#### THERMODYNAMIC PROPERTIES

Tables 26 to 29 summarize the values of the initial contact angle,  $\theta$ , and the calculated values of the surface wetting power,  $\gamma_{LG} \cos \theta$ , the interfacial affinity,  $\gamma_{LG}(1 + \cos \theta)$ , and the work of cohesion for different cationic surfactant concentrations on all the paper samples investigated. The tables are separated for the

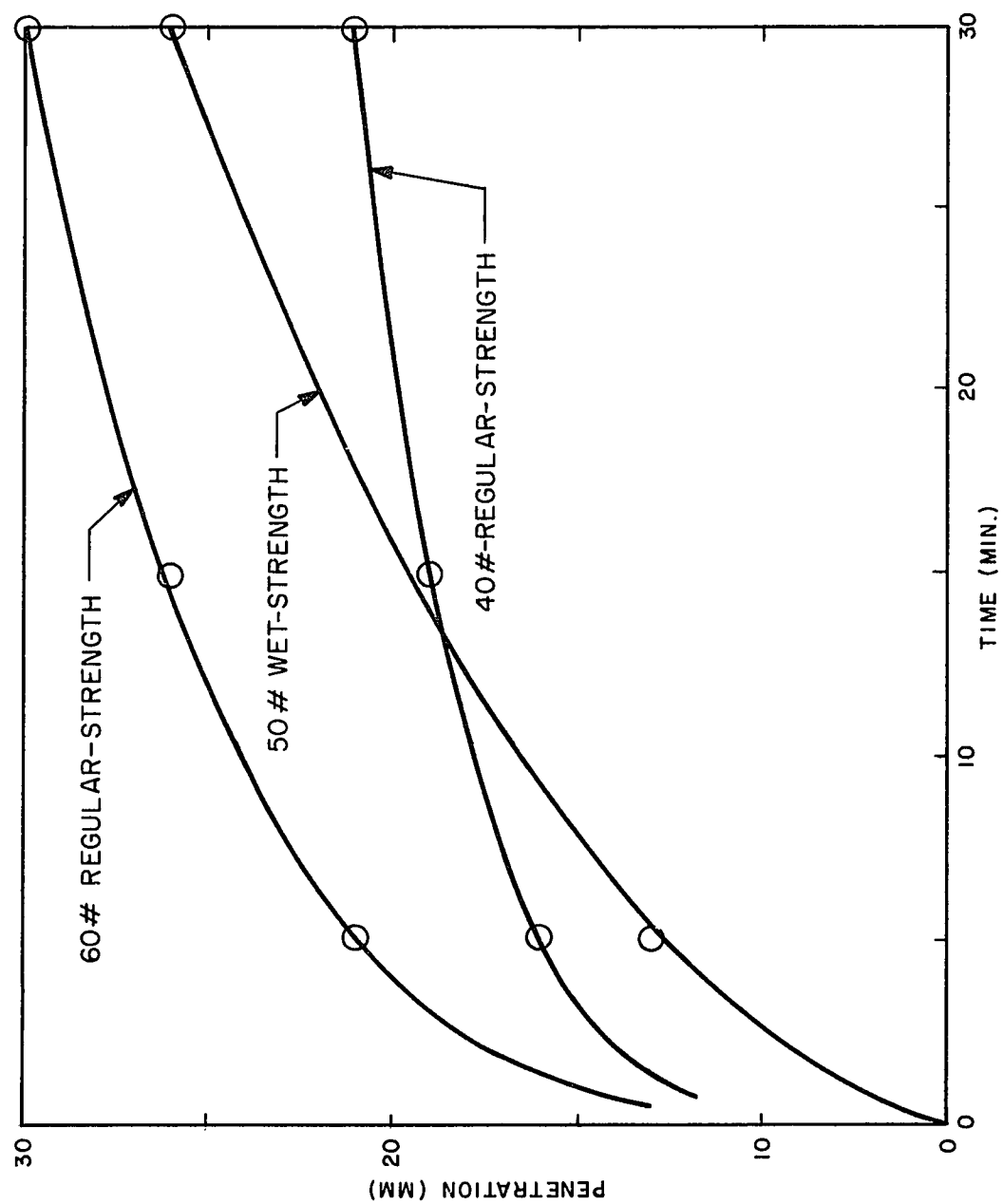


FIGURE 36. CAPILLARY PENETRATION INTO 50-LB, UNBLEACHED, KRAFT SHIPPING SACKS WITH 0.25% ALKYL ARYL SULFONATE

| PAPER<br>SAMPLE | SURFACTANT<br>CONCEN-<br>TRATION | CONTACT<br>ANGLE<br>$\theta$ | SURFACE<br>WETTING           |       | CAPILLARY<br>WETTING          |       | INTERFACIAL<br>AFFINITY<br>$\chi_{LG}(1 + \cos \theta)$ | $W_C$                |
|-----------------|----------------------------------|------------------------------|------------------------------|-------|-------------------------------|-------|---|----------------------|
|                 |                                  |                              | $\chi_{LG}(\cos \theta - 1)$ | POWER | $\chi_{LG} \cdot \cos \theta$ | POWER |   |                      |
|                 | %                                | degrees                      | ergs/cm <sup>2</sup>         |       | dynes/cm                      |       | ergs/cm <sup>2</sup>                                    | ergs/cm <sup>2</sup> |
| Printing        | 0.0                              | 114.1                        | -102.3                       |       | -29.6                         |       | 43.2  | 145.5                |
|                 | 0.005                            | 105.1                        | - 47.9                       |       | - 9.9                         |       | 28.1  | 76.0                 |
|                 | 0.01                             | 95.9                         | - 40.8                       |       | - 3.8                         |       | 33.2  | 74.0                 |
|                 | 0.075                            | 69.6                         | - 23.4                       |       | 12.5                          |       | 48.5  | 72.0                 |
| Catalog         | 0.0                              | 62.5                         | - 39.2                       |       | 33.6                          |       | 106.3   | 145.5                |
|                 | 0.005                            | 58.0                         | - 17.9                       |       | 20.1                          |       | 58.1  | 76.0                 |
|                 | 0.01                             | 57.0                         | - 16.8                       |       | 20.2                          |       | 57.2  | 74.0                 |
|                 | 0.075                            | 37.5                         | - 7.4                        |       | 28.6                          |       | 64.6  | 72.0                 |
| Textweb         | 0.0                              | 71.0                         | - 49.1                       |       | 23.7                          |       | 96.4  | 145.5                |
|                 | 0.005                            | 69.5                         | - 24.7                       |       | 13.3                          |       | 51.3  | 76.0                 |
|                 | 0.01                             | 60.5                         | - 18.8                       |       | 18.2                          |       | 55.2  | 74.0                 |
|                 | 0.075                            | 53.9                         | - 14.8                       |       | 21.2                          |       | 57.2  | 72.0                 |

TABLE 26. SUMMARY OF WETTING CHARACTERISTICS ON GROUNDWOOD PAPERS USING QUATERNARY AMMONIA SURFACTANT

| PAPER<br>SAMPLE  | SURFACTANT<br>CONCEN-<br>TRATION<br>% | CONTACT<br>ANGLE<br>$\theta$<br>degrees | SURFACE<br>WETTING<br>POWER<br>$\chi_{LG}(\cos \theta - 1)$<br>ergs/cm <sup>2</sup> | CAPILLARY<br>WETTING<br>POWER<br>$\chi_{LG} \cos \theta$<br>dynes/cm | INTERFACIAL<br>AFFINITY<br>$\chi_{LG}(1 + \cos^2 \theta)$<br>ergs/cm <sup>2</sup> | $W_C$<br>ergs/cm <sup>2</sup> |
|------------------|---------------------------------------|---|---|--|---|-------------------------------|
| Regular-strength | 0.0                                   | 112.4                                   | -100.5  | -27.7  | 45.0  | 145.5                         |
|                  | 0.01                                  | 106.1                                   | - 47.3  | -10.3  | 26.7  | 74.0                          |
|                  | 0.075                                 | 81.0                                    | - 30.4  | 5.6  | 41.6  | 72.0                          |
|                  | 0.25                                  | 75.2                                    | - 28.3  | 8.9  | 43.9  | 70.0                          |
| Wet-strength     | 0.0                                   | 116.1                                   | -104.8  | -32.0  | 40.7  | 145.5                         |
|                  | 0.01                                  | 103.4                                   | - 45.6  | - 8.6  | 28.4  | 74.0                          |
|                  | 0.075                                 | 73.1                                    | - 25.5  | 10.5   | 46.5  | 72.0                          |
|                  | 0.25                                  | 69.1                                    | - 22.5  | 12.5   | 47.5  | 70.0                          |

TABLE 27. SUMMARY OF WETTING CHARACTERISTICS ON BLEACHED KRAFT PAPERS USING QUATERNARY AMMONIA SURFACTANT

| PAPER<br>SAMPLES | SURFACTANT<br>CONCENTRATION<br>% | CONTACT<br>ANGLE<br>$\theta$<br>degrees | SURFACE<br>WETTING<br>POWER<br>$\chi_{LG}(\cos \theta - 1)$<br>ergs/cm <sup>2</sup> | CAPILLARY<br>WETTING<br>POWER<br>$\chi_{LG} \cos \theta$<br>dynes/cm | INTERFACIAL<br>AFFINITY<br>$\chi_{LG}(1 + \cos \theta)$<br>ergs/cm <sup>2</sup> | $W_C$<br>ergs/cm <sup>2</sup> |
|------------------|----------------------------------|---|---|--|---|-------------------------------|
| 40-1b            | 0.0                              | 107.9                                   | - 95.1  | -22.4  | 50.4  | 145.5                         |
|                  | 0.01                             | 84.0                                    | - 33.1  | 3.9  | 40.9  | 74.0                          |
|                  | 0.075                            | 66.9                                    | - 21.9  | 14.1   | 50.1  | 72.0                          |
|                  | 0.25                             | 56.8                                    | - 15.8  | 19.2   | 54.2  | 70.0                          |
| 50-1b            | 0.0                              | 114.1                                   | -102.4  | -29.7  | 43.0  | 145.5                         |
|                  | 0.01                             | 91.2                                    | - 37.8  | - 1.5  | 36.2  | 74.0                          |
|                  | 0.075                            | 80.8                                    | - 30.2  | 5.8  | 41.8  | 72.0                          |
|                  | 0.25                             | 65.0                                    | - 20.2  | 14.8   | 49.8  | 70.0                          |
| 60-1b            | 0.0                              | 109.9                                   | - 97.5  | -24.8  | 48.0  | 145.5                         |
|                  | 0.01                             | 88.5                                    | - 36.0  | 1.0  | 38.0  | 74.0                          |
|                  | 0.075                            | 67.7                                    | - 22.3  | 13.7   | 49.7  | 72.0                          |
|                  | 0.25                             | 58.5                                    | - 16.7  | 18.3   | 53.3  | 70.0                          |

TABLE 28. SUMMARY OF WETTING CHARACTERISTICS ON UNBLEACHED KRAFT PAPERS USING QUATERNARY AMMONIA SURFACTANT



| PAPER<br>SAMPLES | SURFACTANT<br>CONCEN-<br>TRATION<br>% | CONTACT<br>ANGLE<br>$\theta$<br>degrees | SURFACE<br>WETTING<br>POWER<br>$\chi_{LG}(\cos \theta - 2)$<br>ergs/cm <sup>2</sup> | CAPILLARY<br>WETTING<br>POWER<br>$\chi_{LG} \cos \theta$<br>dynes/cm | INTERFACIAL<br>AFFINITY<br>$\chi_{LG}(1 + \cos \theta)$<br>ergs/cm <sup>2</sup> | $W_C$<br>ergs/cm <sup>2</sup> |
|------------------|---------------------------------------|---|---|--|---|-------------------------------|
| Foodboard        | 0.0                                   | 111.0                                   | -98.8   | -26.0  | 46.7  | 145.5                         |
|                  | 0.01                                  | 91.0                                    | -37.6   | - 0.6  | 36.4  | 74.0                          |
|                  | 0.075                                 | 74.8                                    | -26.6   | 9.4  | 45.4  | 72.0                          |
|                  | 0.25                                  | 61.1                                    | -18.1   | 16.9   | 51.9  | 70.0                          |
| Bond             | 0.0                                   | 105.2                                   | -91.8   | -19.1  | 53.7  | 145.5                         |
|                  | 0.01                                  | 105.0                                   | -46.6   | - 9.6  | 27.4  | 74.0                          |
|                  | 0.075                                 | 80.1                                    | -29.8   | 6.2  | 42.2  | 72.0                          |
|                  | 0.25                                  | 70.8                                    | -23.5   | 11.5   | 46.5  | 70.0                          |

TABLE 29. SUMMARY OF WETTING CHARACTERISTICS ON BLEACHED SULFITE PAPERS USING QUATERNARY AMMONIA SURFACTANT

groundwood, bleached kraft, unbleached kraft, and sulfite group of paper samples.

The values of capillary penetration squared have been plotted against time for the catalog and textweb groundwood samples. The liquids used were water and the quaternary ammonium surfactant. The results are shown in Figure 37.

The surface wetting powers have been plotted against the average detention time using the quaternary ammonia surfactant. The results are shown in Figures 38 to 41. These figures are separated for the groundwood, bleached kraft, bleached sulfite, and unbleached kraft paper samples.

#### PAPER SHAPE EFFECTS

##### Detention Times

Detention times were studied using regular and irregular paper shapes and various concentrations of surfactants. The bleached regular-strength kraft shipping sack was used throughout this phase of the investigation. The surfactant selected was the long-chained polyoxyethylene combination fatty amine and sorbitol oleate (Atlas G-2090). It was diluted with deionized water to form concentrations of 0.01, 0.05, and 0.10 percent.

The detention times using the 0.10% cationic syndet are shown for the various paper shapes in Table 30. The first two columns show that initially five chips of each of the regular shapes and fourteen irregularly shaped ships were scattered over the liquid sur-

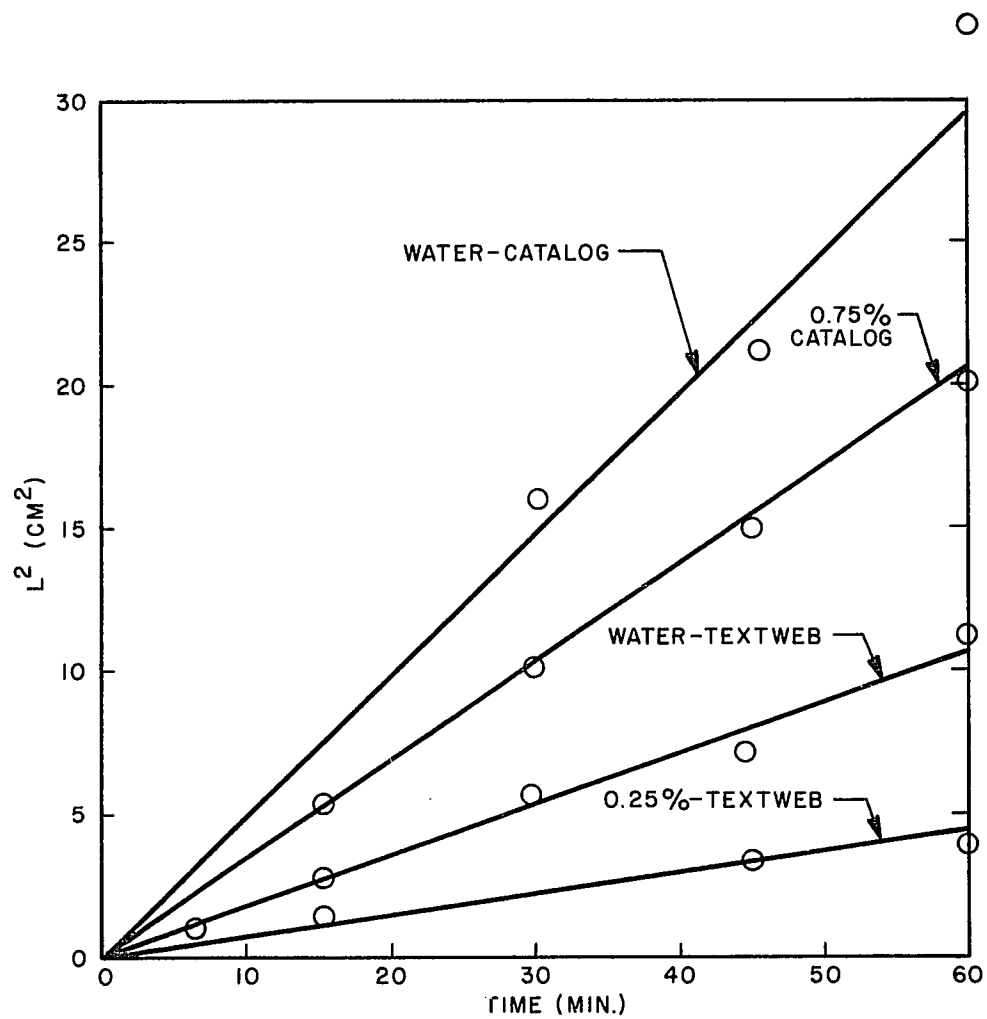


FIGURE 37. PROPORTIONALITY BETWEEN  $L^2$  AND T FOR GROUNDWOOD PAPERS USING QUATERNARY AMMONIA SURFACTANT & WATER

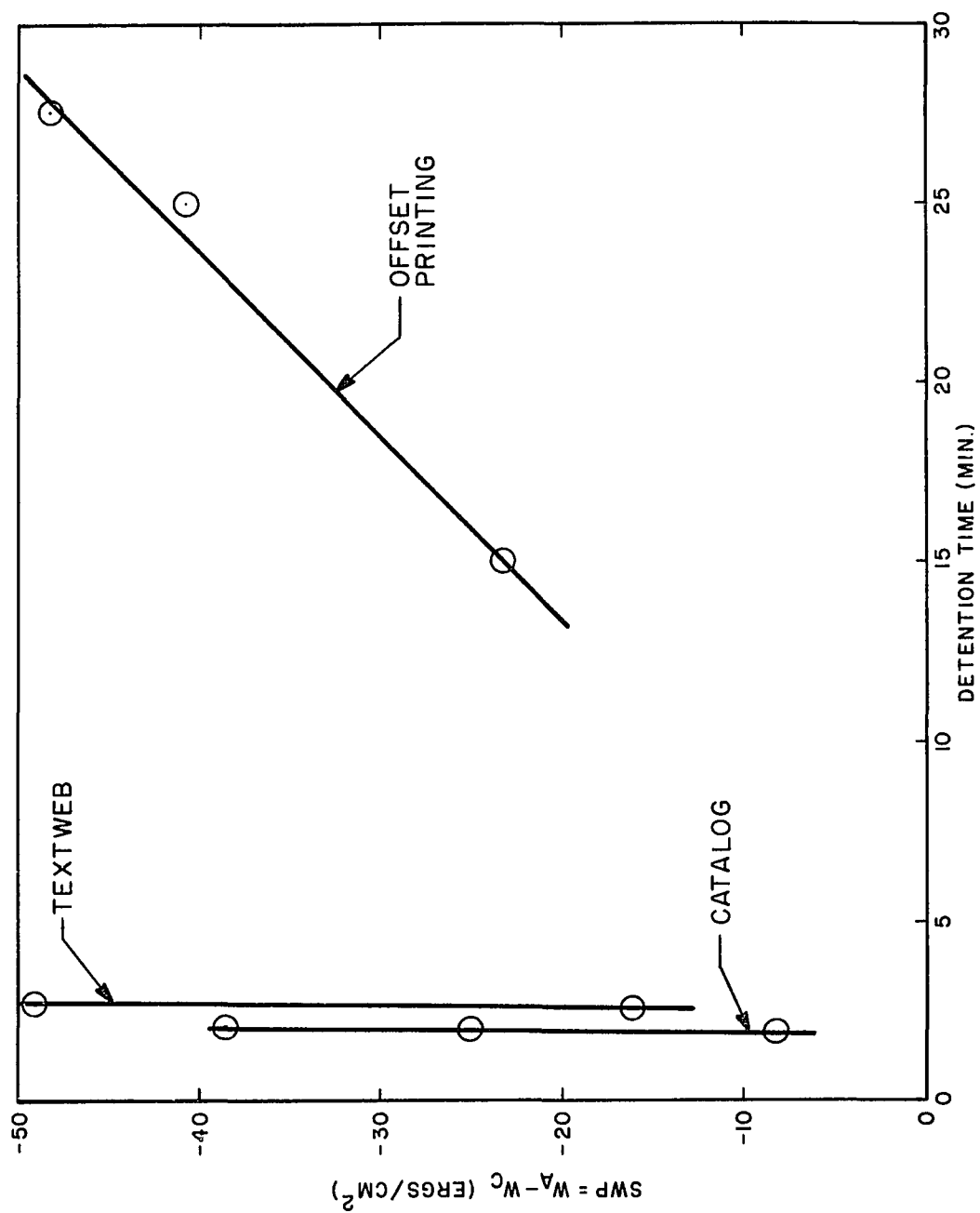


FIGURE 38. SURFACE WETTING POWER VS AVERAGE DETENTION TIME FOR GROUNDWOOD PAPERS USING QUATERNARY AMMONIA SURFACTANT

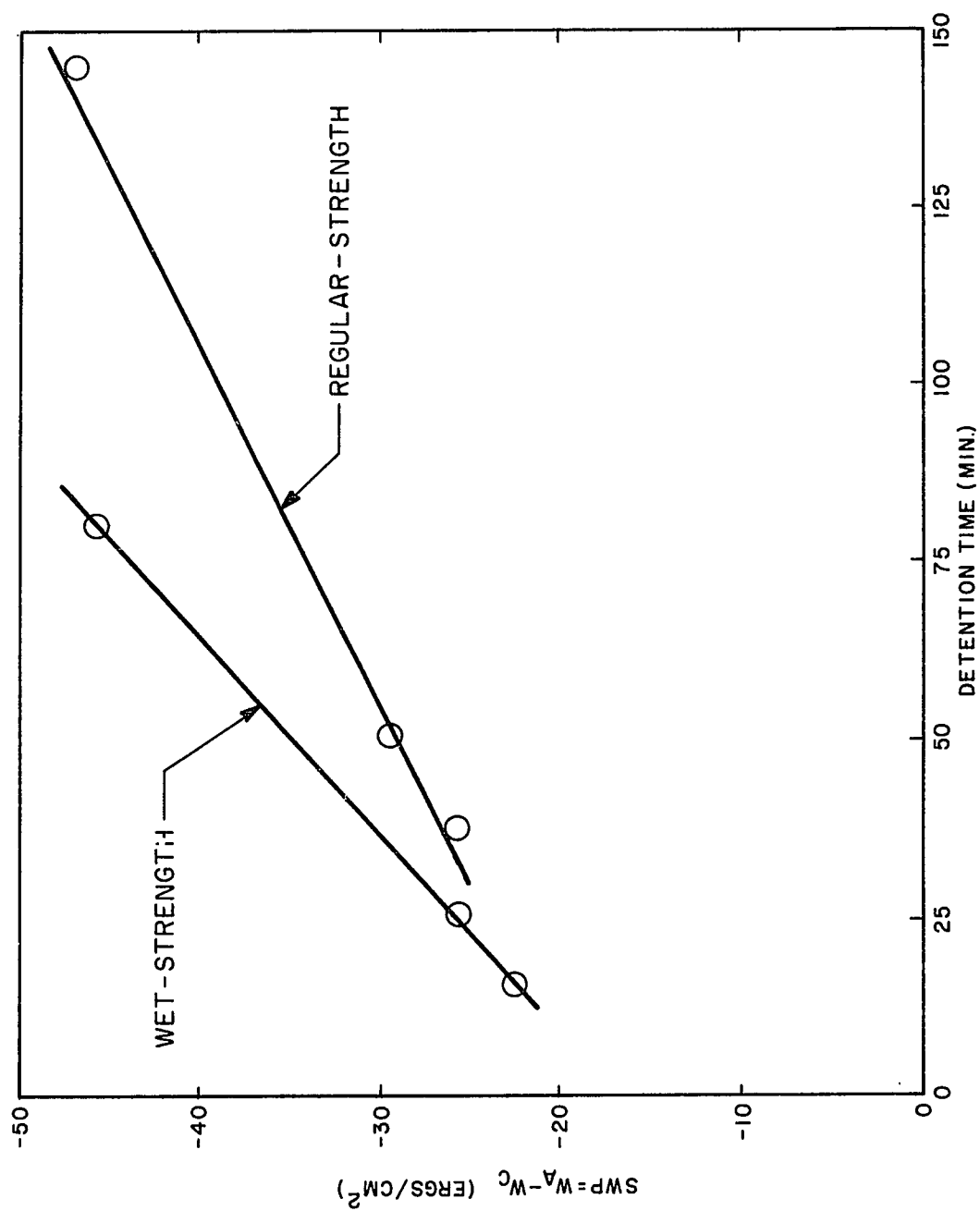


FIGURE 39. SURFACE WETTING POWER VS AVERAGE DETENTION TIME FOR BLEACHED KRAFT PAPERS USING QUATERNARY AMMONIA SURFACTANT

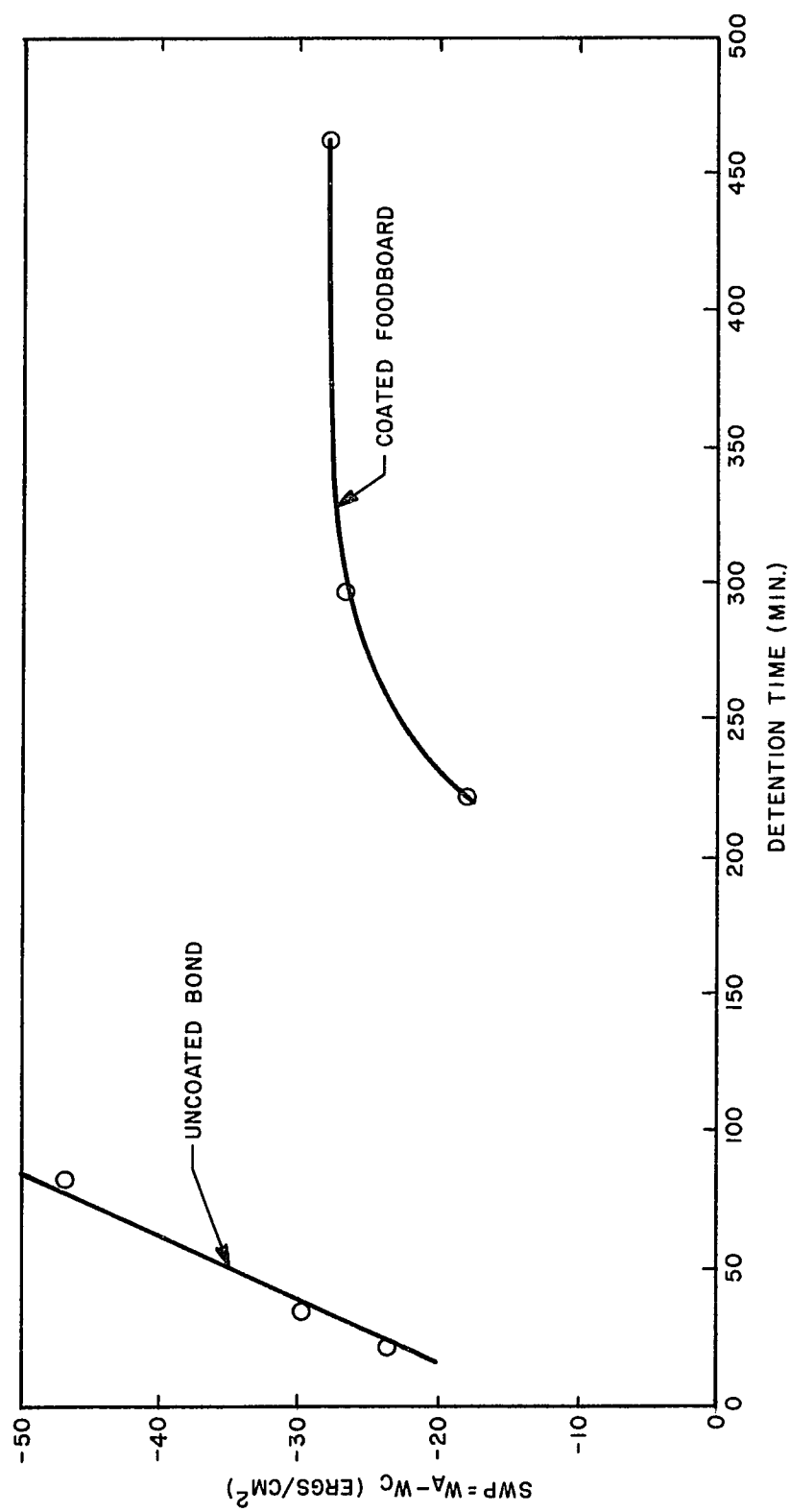


FIGURE 40 SURFACE WETTING POWER VS AVERAGE DETENTION TIME FOR BLEACHED SULFITE PAPERS USING QUATERNARY AMMONIA SURFACTANT

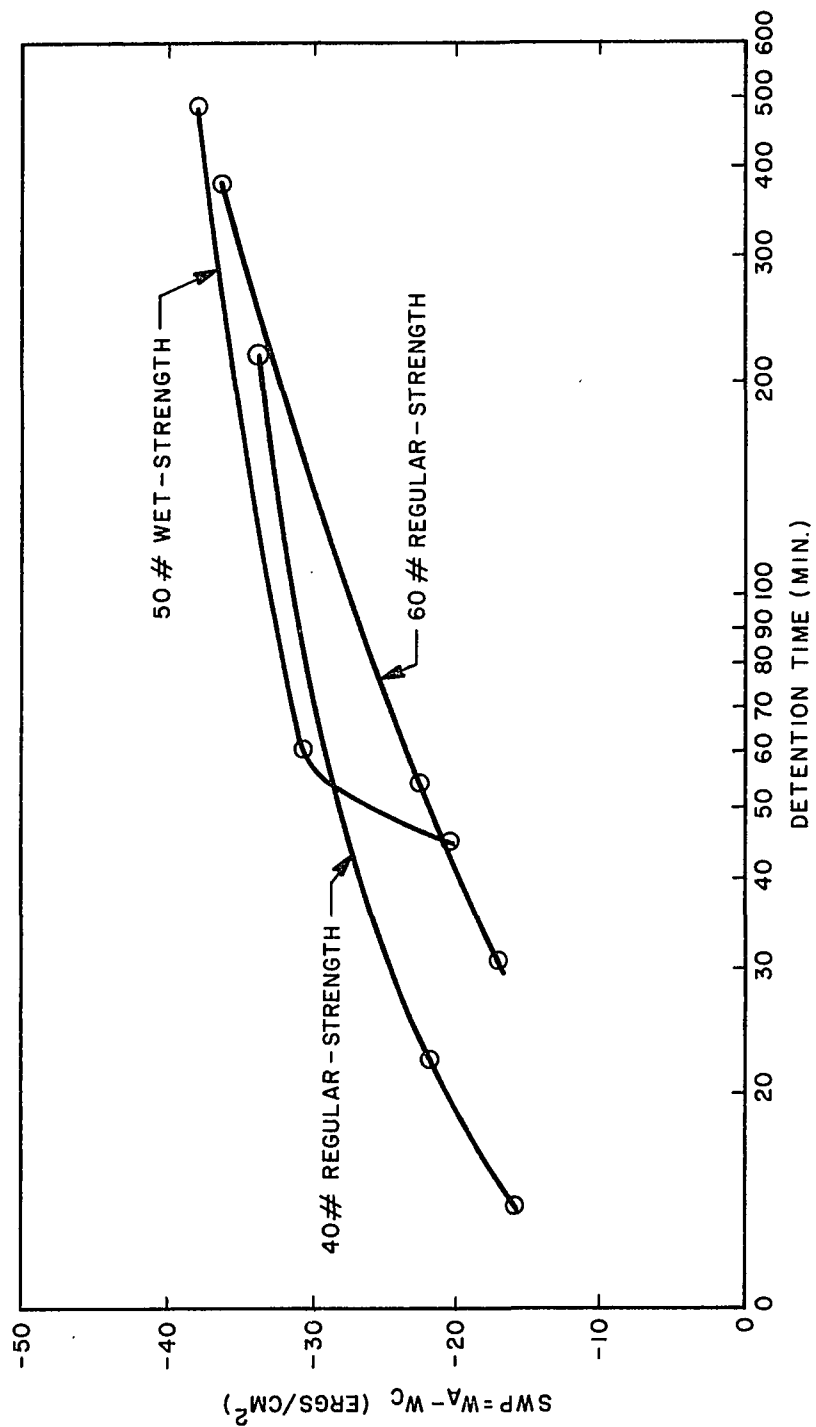


FIGURE 41. SURFACE WETTING POWER VS AVERAGE DETENTION TIME FOR UNBLEACHED KRAFT PAPERS USING QUATERNARY AMMONIA SURFACTANT

| Shape     | Size               | No.<br>Chips | Time (Minutes) |    |    |    |    |    |    |     |     |     |     |     |     |  |  |  |
|-----------|--------------------|--------------|----------------|----|----|----|----|----|----|-----|-----|-----|-----|-----|-----|--|--|--|
|           |                    |              | 0              | 20 | 30 | 45 | 60 | 75 | 90 | 105 | 120 | 135 | 150 | 165 | 180 |  |  |  |
| Square    | $\frac{1}{2}$ "    | 5            | 5              | 5  | 5  | 5  | 4  | 4  | 3  | 2   | 2   | 0   | -   | -   | -   |  |  |  |
|           | 1"                 | 5            | 5              | 5  | 5  | 5  | 5  | 4  | 4  | 2   | 1   | 0   | -   | -   | -   |  |  |  |
|           | $1\frac{1}{2}$ "   | 5            | 5              | 5  | 5  | 5  | 4  | 4  | 3  | 3   | 3   | 2   | 1   | 1   | 0   |  |  |  |
|           | 3"                 | 5            | 5              | 5  | 5  | 5  | 5  | 5  | 4  | 3   | 3   | 0   | -   | -   | -   |  |  |  |
| Circle    | 1"                 | 5            | 5              | 5  | 5  | 5  | 5  | 5  | 5  | 3   | 2   | 1   | 0   | -   | -   |  |  |  |
|           | 2"                 | 5            | 5              | 5  | 5  | 4  | 4  | 4  | 3  | 3   | 3   | 1   | 0   | -   | -   |  |  |  |
|           | 3"                 | 5            | 5              | 5  | 4  | 4  | 4  | 4  | 4  | 3   | 1   | 1   | 1   | 0   | -   |  |  |  |
| Irregular | $\frac{1}{2}$ "-3" | 14           | 14             | 14 | 14 | 14 | 12 | 12 | 10 | 6   | 3   | 2   | 2   | 0   | -   |  |  |  |

TABLE 30. DETENTION TIMES FOR VARIOUS SHAPES OF 50-LB, BLEACHED, KRAFT SHIPPING SACK USING 0.10% FATTY AMINE AND SORBITOL OLEATE SURFACTANT



face. Within the table are recorded the number of chips that have remained floating at the specific detention time.

The first paper to wet and sink was a 3-inch circle which had been in contact with the wetting liquid for 30 minutes. The first 0.5 and 1.5 inch squares and two irregular shaped chips began to sink after 60 minutes. Only two square, three circular, and two irregular chips are still floating after 135 minutes.

The results from this table were used to construct a cumulative percentage removal curve versus detention time shown in Figure 42. This curve shows that the paper chips started to sink after twenty minutes and all had sunk after 180 minutes. The steepest portion of the curve shows that 72% of the papers are removed over the sixty minute period between the 75 and 135 minute detention times. The curve also shows that 110 minutes, between the 47 and 157 minute detention times, are required to remove 90% of all the various paper shapes.

#### Settling Rates

To determine paper shape effects on settling characteristics, a clear plexiglass column was filled with a 0.01% concentration of the previous cationic surfactant. The bleached regular-strength kraft shipping sack was used to form different sizes of circles and squares. The chips were allowed to float on the surface where primary wetting occurred. After the chips began to settle, the elapsed times for them to fall every six inches was recorded until they reached the bottom. The different rates of descent can be seen.

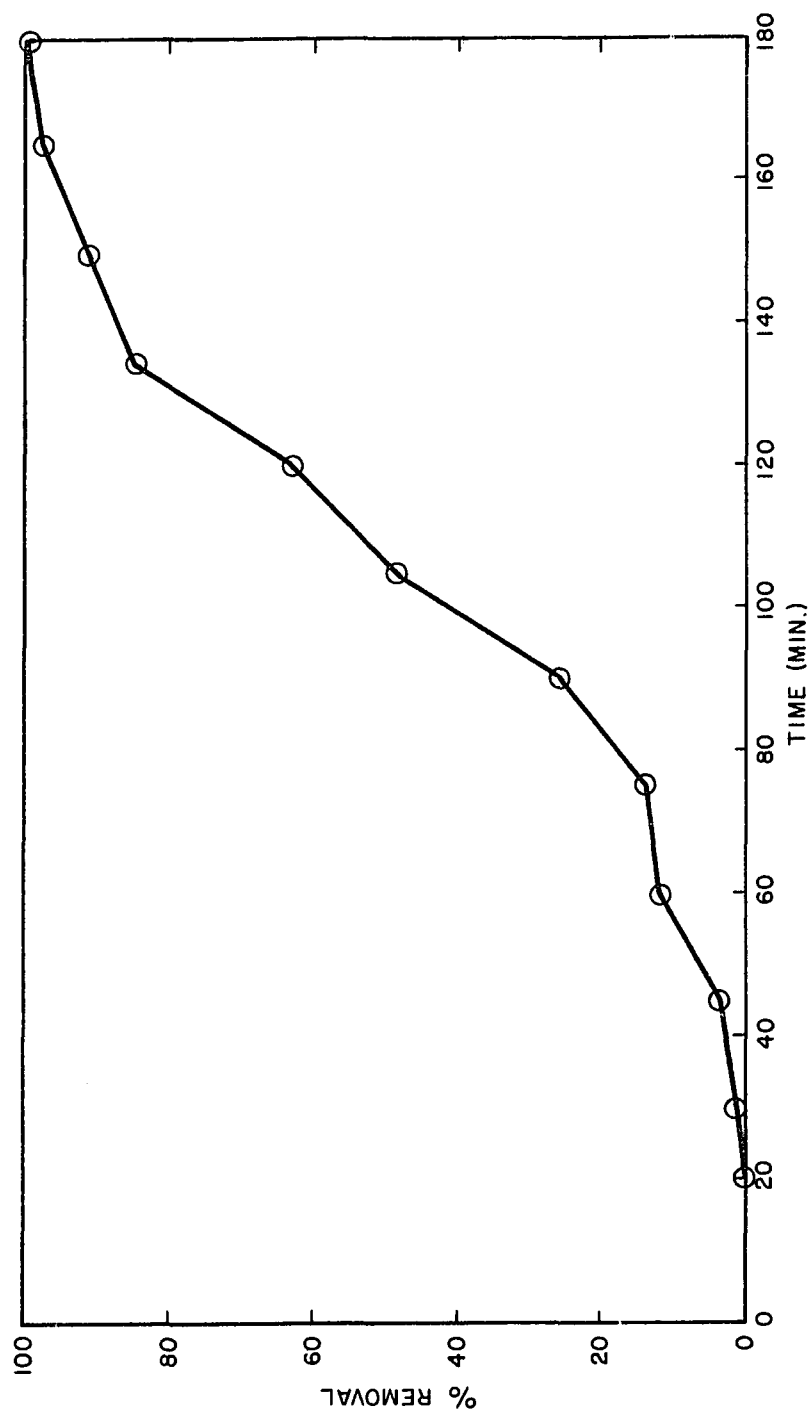


FIGURE 42. RECOVERY OF VARIOUS SHAPES OF 50-LB BLEACHED, KRAFT SHIPPING SACK USING 0.01% FATTY AMINE AND SORBITOL OLEATE SURFACTANT

Although several determinations were made with one-inch diameter circles, only the fastest and slowest settling curves are shown in Figure 43. The average rate of descent for the slowest chip is 0.025 feet per second. The fastest chip fell with an average speed of 0.053 feet per second. It can be seen from the curves that the settling rates increase as the chips approach the tank bottom. Clinging air bubbles were observed to be dislodged as the chips started to sink so that the individual buoyancies were reduced.

Similarly, the fastest and slowest settling curves for one-inch square chips are shown in Figure 44. The average settling rates vary from 0.029 to 0.069 feet per second. Here also the settling rates can be seen to increase as it descends in the column. The flattest portion for the initial rate is close to 0.023 feet per second; the steepest portion near the bottom is 0.125 feet per second.

#### CONTINUOUSLY MIXED PILOT PLANT

The paper samples that were studied throughout this phase of work included all five kraft shipping sacks of various sizes. They included bleached and unbleached, wet-strength and regular-strength, and different weighted papers. Because of the distinct economic value of the bleached fibers over the unbleached fibers, a recovery system was developed for this separation. Based on the quiescent recovery results and the detention times for these samples, a cationic surfactant was selected. The one used was a heterocyclic tertiary amine (Ciba-Geigy Amine T).

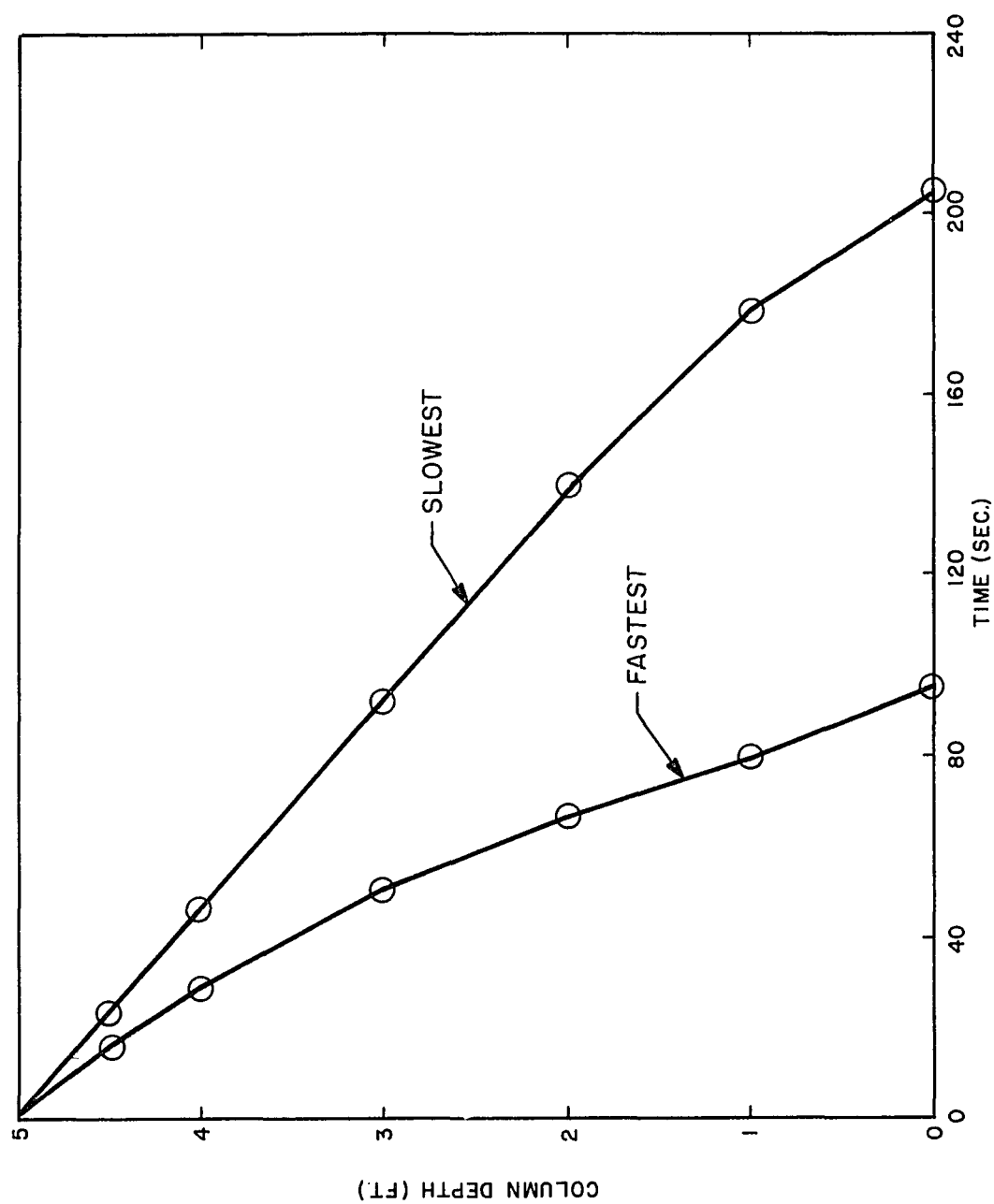


FIGURE 43. SETTLING CURVES FOR ONE-INCH DIAMETER CIRCLES OF 50-LB, BLEACHED, KRAFT SHIPPING SACK USING 0.01% FATTY AMINE AND SORBITOL OLEATE SURFACTANT

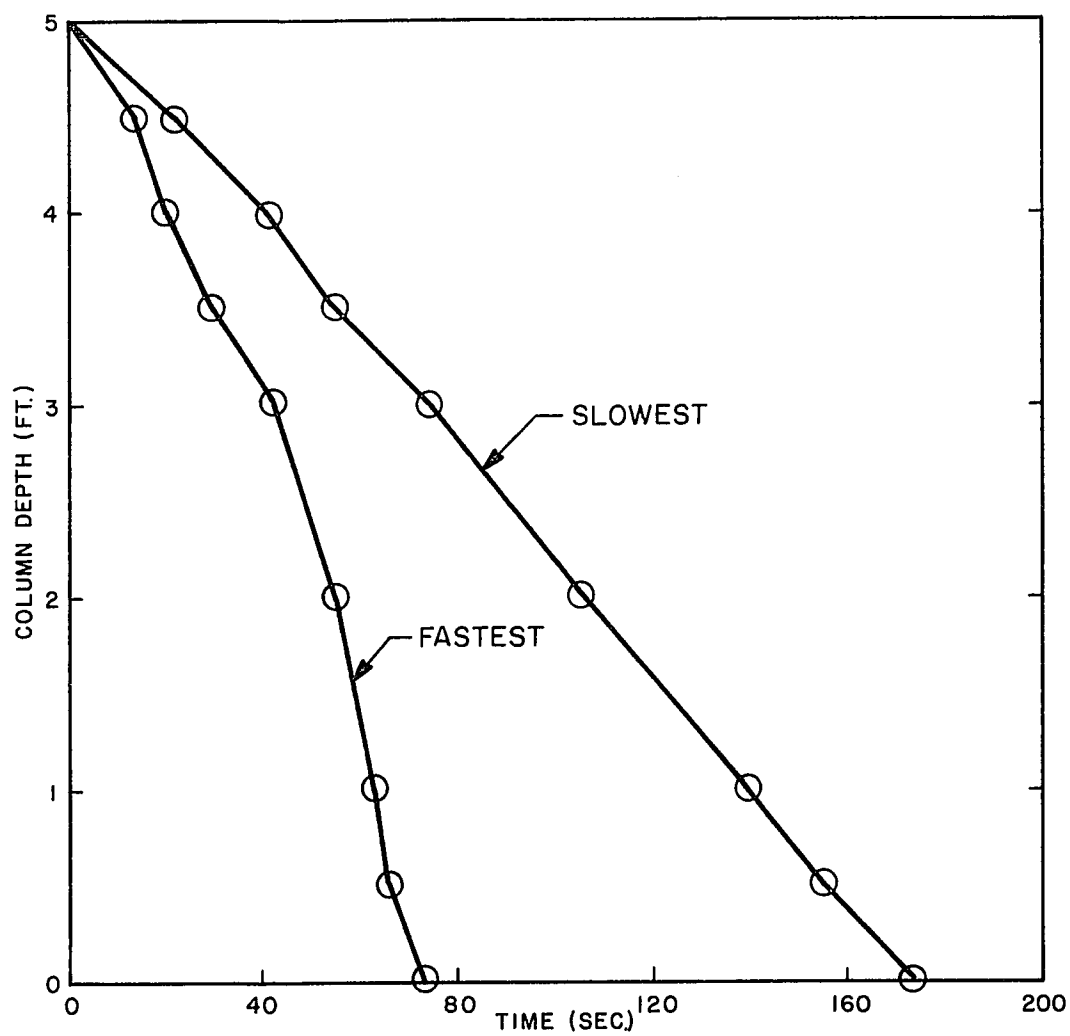


FIGURE 44. SETTLING CURVES FOR ONE-INCH SQUARES OF 50-LB, BLEACHED, KRAFT SHIPPING SACK USING 0.01% FATTY AMINE AND SORBITOL OLEATE SURFACTANT

### Recovery Results

To determine the effects of mixing and detention times, different loads of the bleached and unbleached were subjected to various mixing speeds. The detention times for the combined bleached grades, 50 grams each, at different mixing speeds are shown in Figure 45. This figure plots the percentage of the samples, by weight, which have been recovered during this operation using 0.01% concentration of the surfactant. At a mixing speed of 62 rpm, all 100 grams of the bleached chips were recovered from the tank bottom in only 35 minutes. The curve for the mixing speed of 32 rpm indicates that all the samples were removed in 57.5 minutes. The last curve represents the results from the previous quiescent recovery determinations for a comparison. For this low loading rate without any mixing, a detention time of 75 minutes was required to recover all of these samples.

Figure 46 compares the recovery detention times at a constant mixing speed of 32 rpm for the individual samples. The detention time for the recovery curve of the bleached samples has already been mentioned. The results for the light weight unbleached kraft sack will be presented. To achieve a 90% removal of this sample required 75 minutes of mixing. A detention time of nearly 150 minutes was required to achieve this level when this sample was subjected to quiescent wetting. For a fifty gram loading for each of the other unbleached sacks one can see that only 5% are removed in 90 minutes of mixing. Under quiescent conditions a detention time of 6 hours was needed to recover all of these samples.

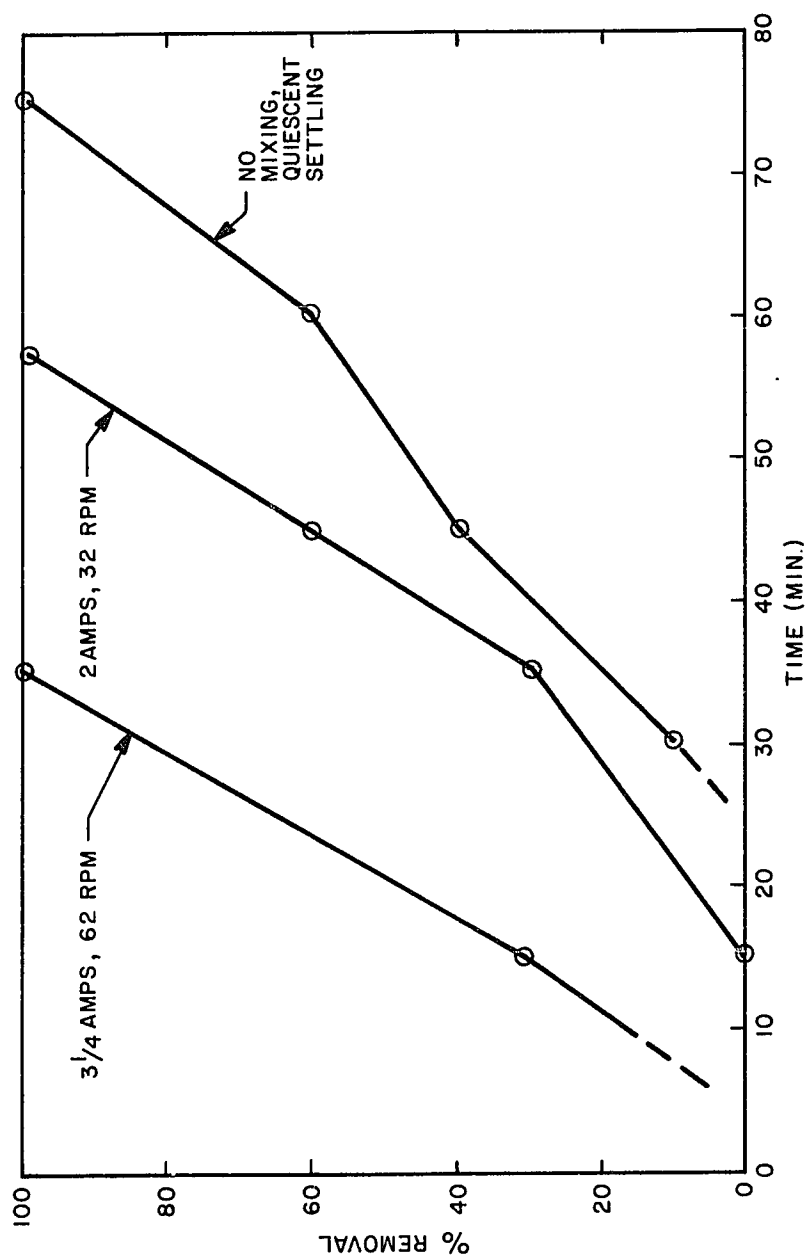


FIGURE 45. RECOVERY CURVES OF 50-LB. BLEACHED, KRAFT SHIPPING SACK FOR DIFFERENT MIXER SPEEDS USING 0.01 % HETEROCYCLIC TERTIARY AMINE SURFACTANT

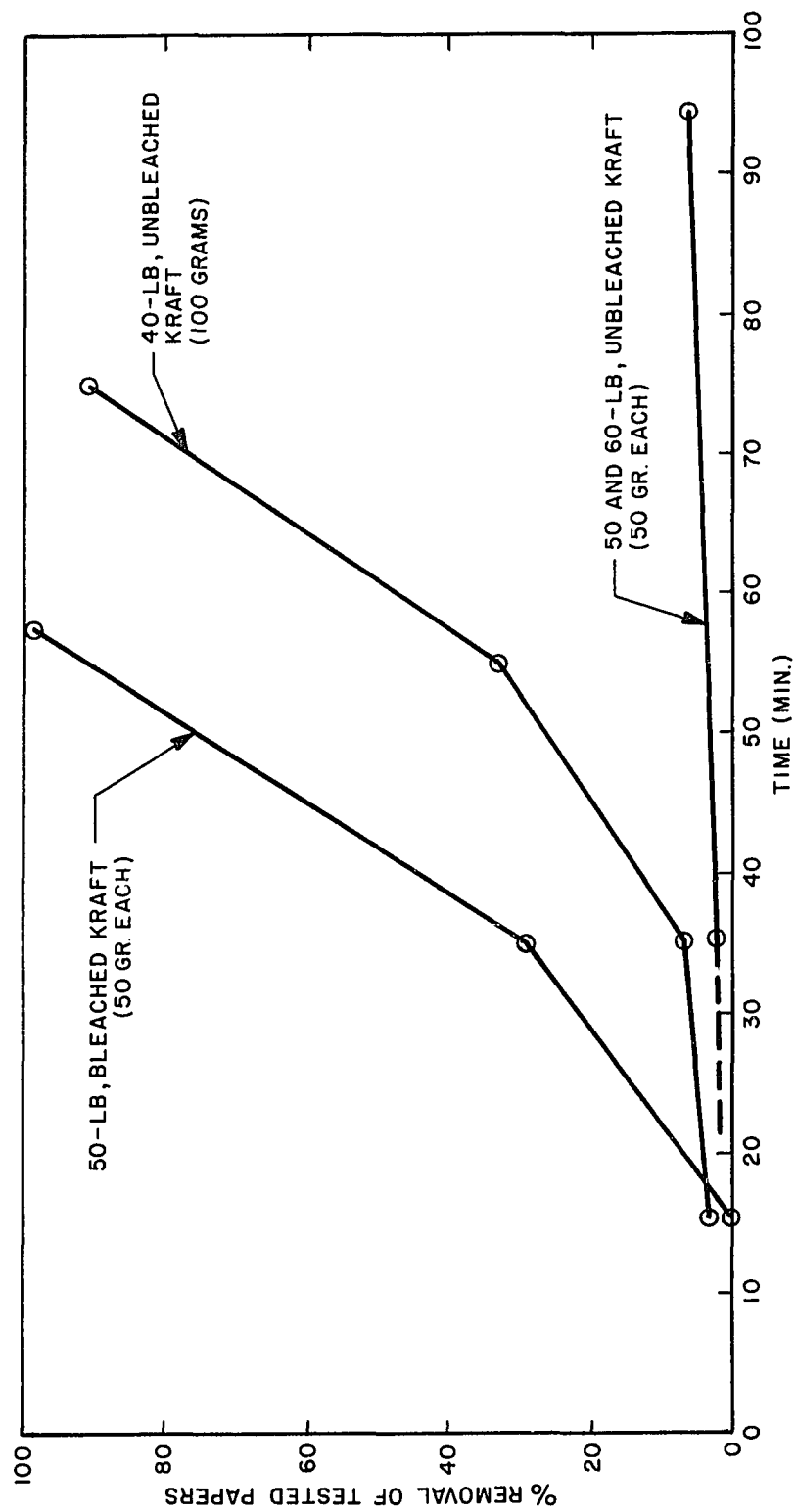


FIGURE 46. RECOVERY CURVES FOR MIXED BATCH SYSTEM USING 0.01% HETEROCYCLIC TERTIARY AMINE SURFACTANT (MIXER AT 32 RPM, 2 APMS)



### Operational Results

After the detention times for the separate samples had been determined for different mixing speeds, it was decided to determine loading rates and power requirements with batch applications. Equal weights of all five samples were introduced into the tank containing the amine surfactant at the 0.01% concentration level and the detention times for removal of the bleached samples were determined after continuously mixing the entire batch.

The operating curves for the batch recovery system at a constant mixing speed of 32 rpms at 2.0 amps are shown in Figure 47. The first curve for a total batch load of 350 grams shows that approximately 90 minutes were required to recover 90% of all the bleached kraft paper. The next graph for 100 grams each, or 500 grams of total load, indicates that close to 130 minutes were needed to achieve this same level of recovery.

Based upon the batch operating curves, the loading rates for achieving 90% recovery of the bleached papers have been determined. At this level some of the light-weight unbleached sack were also recovered but most of the papers collected were the bleached papers.

These values are summarized along with the power requirements in Table 31. The first column shows the total batch weight of all five kraft samples. The second column lists the detention time required to remove 90% of all the bleached papers. The next two columns show the power requirements to treat one pound of the batch of papers.

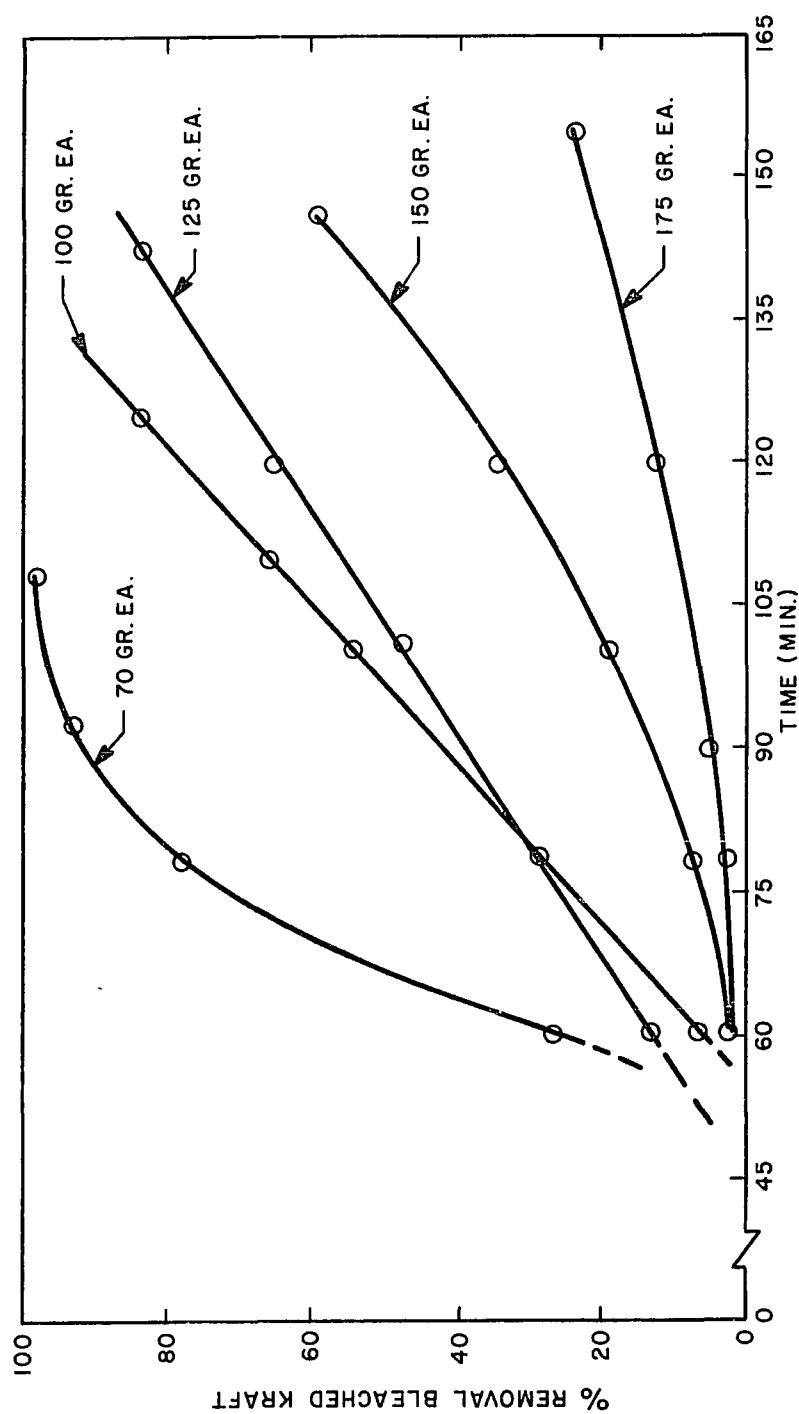


FIGURE 47. OPERATING CURVES FOR CONTINUOUSLY MIXED PILOT PLANT TO RECOVER BLEACHED KRAFT USING 0.01% HETEROCYCLIC TERTIARY AMINE SURFACTANT (MIXER AT 32 RPM, 2 AMPS)

| WEIGHT OF<br>BATCH,<br>(gm) | DETENTION TIME FOR<br>90% RECOVERY,<br>(min) | LOADING<br>RATE,<br>(lb/ft <sup>2</sup> /day) | LOADING<br>RATE,<br>(lb/1000 gal/day) | POWER<br>REQUIREMENT<br>(kw-hr/lb) |
|-----------------------------|--|---|---------------------------------------|------------------------------------|
| 350                         | 90   | 1.54  | 91.6                                  | .466                               |
| 500                         | 130  | 1.52  | 90.5                                  | .473                               |
| 625                         | 150  | 1.65  | 98.2                                  | .435                               |
| 750*                        | 170  | 1.74  | 103.9                                 | .412                               |
| 875                         | 240  | 1.44  | 85.7                                  | .499                               |

\*OPTIMUM PERFORMANCE FOR BATCH PLANT SYSTEM OPERATING AT 32RPM WITH 0.01%  
HETEROCYCLIC TERTIARY AMINE

TABLE 31. LOADING RATES AND POWER REQUIREMENTS TO RECOVER 90% BLEACHED KRAFT SACKS  
USING THE BATCH PLANT SYSTEM

## V DISCUSSION

### QUIESCENT DETENTION TIMES AND PAPER GRADE RECOVERY

The results of the quiescent detention times and paper grade recoveries indicate that most paper additives and coatings which are applied to the pulp or to the finished papers tend to resist water wetting. Consequently, while cellulose and most of the other components in paper have a specific gravity greater than 1.00, the pore spaces between the fibers, being filled with air, cause individual paper sheets to float on water for some finite time. Liquids, in time, will penetrate the pores sufficiently to dispel enough trapped air to cause the sheets to sink. While water can be used to achieve desirable recovery groups, the detention times to wet the papers are excessive and would seriously limit its application on an industrial scale operation.

All surfactants can be used to effectively separate groundwood from non-groundwood papers and coated from uncoated papers. While all detention times are lowered using any surfactant, ionic wetting agents, at specific low concentrations, can be effectively used to regulate and control the sinking times so that many paper grades can be selectively and desirably separated. Some separations can be

achieved with non-ionics but they showed little ability to separate bleached from unbleached papers.

The results further indicate that differences occurred according to the charge of the ionic species. Cationic surfactants resulted in the papers wetting in order of groundwood, bleached fibers, and unbleached shipping sacks. Different results occurred with the other ionic surfactants. Because of the opposite charge, the anionic species all tended to wet the bleached ones. The non-ionic surfactant resulted in extreme variations within this specific group of papers and could not be effectively applied to a paper recycling system based upon the selective wettability process. The results also indicate that, within a charge group, better separations, over workable detention times, can be achieved with a specific type of surfactant.

### Water

Water can be used to achieve desirable paper recovery groups under quiescent conditions. Most groundwoods are wetted immediately, in Table 10, with the starch surface-sized sample requiring 72 hours to entirely sink to the tank bottom. A high percentage of these chips are however wetted in one and a half hours, so that, in this time, most groundwoods could be separated from the chemically produced papers.

Another desirable recovery group which could be achieved with a long detention time using water would be the separation between the bleached and unbleached papers. Based on these samples and a

detention time of three days, the majority of the bleached paper samples would wet and sink leaving the majority of the unbleached papers still floating. The bleached coated foodboard sample also remains floating and could not be collected with the other bleached papers.

Based on these results, water can not be used to effectively separate papers according to their basis weights or coated from uncoated ones. The use of water for achieving any of the desirable separations requires extensive detention times which would severely limit its industrial applications.

#### Cationic Surfactants

Because of the long detention times using water to achieve desirable paper recovery groups, several long-chain cationic surface-active agents were studied to determine the effects of reducing the times, and also, to establish other possible recovery groups that could be achieved from the selected grades. Table 11 indicates an efficient separation between bleached and unbleached papers can be achieved in 2.5 hours. By this time the bleached papers have become wet and sunk. This is still 30 minutes before the unbleached 40# shipping sack starts to sink. By the time the majority of the unbleached samples have sunk, the eighth hour, most of the wax-coated bleached paper chips are still floating. This sample could be removed by skimming the surface to collect it before all chips sank at the tenth hour.

From Table 12 it can be seen that all wetting rates are so drastically accelerated that the only desirable recovery groups would be

between coated and uncoated papers. This separation occurs by an hour and a half leaving only the coated foodboard on the liquid surface.

At high concentrations while all detention times are greatly reduced, the times were so rapid that no recovery groups could be established. For instance, the use of most of the surfactants at the 0.50% level resulted in immediate wetting and sinking of the samples.

An inspection of the other quiescent detention times and paper recovery groups, shown in Tables 13 to 15, shows that cationic surfactants in low concentrations can be used to effectively separate groundwoods from chemically produced papers, bleached from unbleached papers, and coated from uncoated papers. Also these desirable separations can all be efficiently achieved within reasonable detention times.

#### Anionic Surfactants

While all individual detention times are lower using anionic surfactants rather than water, these surfactants can also be used to achieve many desirable recovery groups. Table 16 indicates that a large portion of the unbleached papers could be wetted before all of the bleached sacks sank. By the sixth hour most of the unbleached sacks have sunk leaving most of the bleached papers still floating. By the time these bleached papers have sunk, at the eleventh hour, all the coated foodboard chips are still on the liquid surface where they can be easily removed and recovered.

Excellent wetting and recovery groups are indicated in Table 17 for alkyl aryl sulfonate. Again, the groundwoods are all easily removed in a detention time of 20 minutes. The results at the tenth hour also indicated that good separations can be achieved between the bleached and unbleached kraft sacks. At this detention time most of the unbleached shipping sacks have sunk leaving most of the bleached ones still on the surface. The last column again shows that all the coated chips will still be floating after all other samples are at the tank bottom, where they can easily be recovered.

An examination of the detention times shown in Tables 18 and 19 shows that these surfactants can also be used to achieve desirable recovery groups within the selected paper samples. These major groups in the order of accelerated wetting, include all groundwoods, the bleached bond, unbleached kraft, and bleached kraft. Finally, the coated food-board remains the least susceptible to wetting and stays floating. As in the case of the cationic surfactants, these desirable separations can be achieved within reasonable detention times.

#### Non-ionic Surfactants

When the detention times were determined using the non-ionic surfactants, it was found that the wetting was accelerated compared to using water as the wetting liquid. However these surfactants all showed severe limitations in achieving desirable recovery groups with these samples. The detention times shown in Table 20 indicate severe overlapping of the bleached and unbleached papers so that they cannot be readily separated using this tridecyl ether surfactant. The results at the fourth hour show that it can be used to separate effectively close to all coated from uncoated papers.

Table 21 shows similar separating limitations from results of using a monolaurate. This surfactant can effectively separate the groundwoods from the other samples and the coated from the uncoated, but little else. Between the first and the sixth hour one can see that the paper samples are indiscriminately wetting and sinking without forming any desirable groups. The uncoated bleached papers are sinking along with the unbleached sacks resulting in a heterogeneous



mixture at the bottom of the tank.

The results using the coconut fatty acid, in Table 22, show very similar results. It can be used to separate groundwoods and coated papers, but most of the wetting of the other samples occurs simultaneously over narrow detention times. For this surfactant, most of the mixed wetting occurs between 1 and 2.25 hours.

#### LABORATORY BENCH SCALE WETTING

Because of the results obtained from the quiescent detention times and the paper grade recovery groups, the principle parameters which governed the wetting processes for the samples were studied. The diversification of the samples made many comparisons possible. For instance, within the groundwood group of papers, comparing the effects of coated against uncoated papers and differences between internal and surface sizing agents could be made. The bleached krafts offered an opportunity to isolate a wet-strength additive in one sample against the regular-strength properties of another. The unbleached krafts not only could be compared to the bleached sacks but, also, made it possible to study the wetting effects due to different basis weights. The other group of papers included two sulfites, one of which was a heavy wax coated foodboard while the other was an uncoated bond.

The basic thermodynamic principles of the wetting processes were explored using a cationic, the quaternary ammonium derivative, and an anionic surfactant, the alkyl aryl sulfonate. The measurements made with these syndets and the paper samples included surface ten-

sions, transient contact angles, and capillary penetrations. The surface and capillary wetting powers, along with the interfacial affinities and works of cohesion, are summarized and discussed for the quaternary ammonia surfactant and the paper samples.

### Surface Tensions

The surface tensions determined for the quaternary ammonium derivative and the alkyl aryl sulfonate surfactants indicate significant reductions compared to that of water. The reduction of the surface tensions accelerated all recovery times of the paper samples compared to the water recovery results by lowering the interfacial affinities and the free energies. Fischer and Gans studied the range of values for the interfacial tension between aqueous commercial surfactants and mineral oils.<sup>(74)</sup> Their results for the majority of surface-active agents at various concentrations can be seen within the shaded area in Figure 48. Practically all the detergents reduce the surface tension of water to values between 26 and 38 dynes/cm. This figure shows that the greatest change is reached after a concentration of about 0.20 percent without any appreciable reduction occurring at higher concentrations. The average value for the surface tension of an average surface-active agent at the 0.20 percent concentration is about 32 dynes/cm. The values obtained for the tested surfactants in this study lie between this shaded area showing good agreement with their work.

### Transient Contact Angles

Some general remarks can be made concerning all these transient

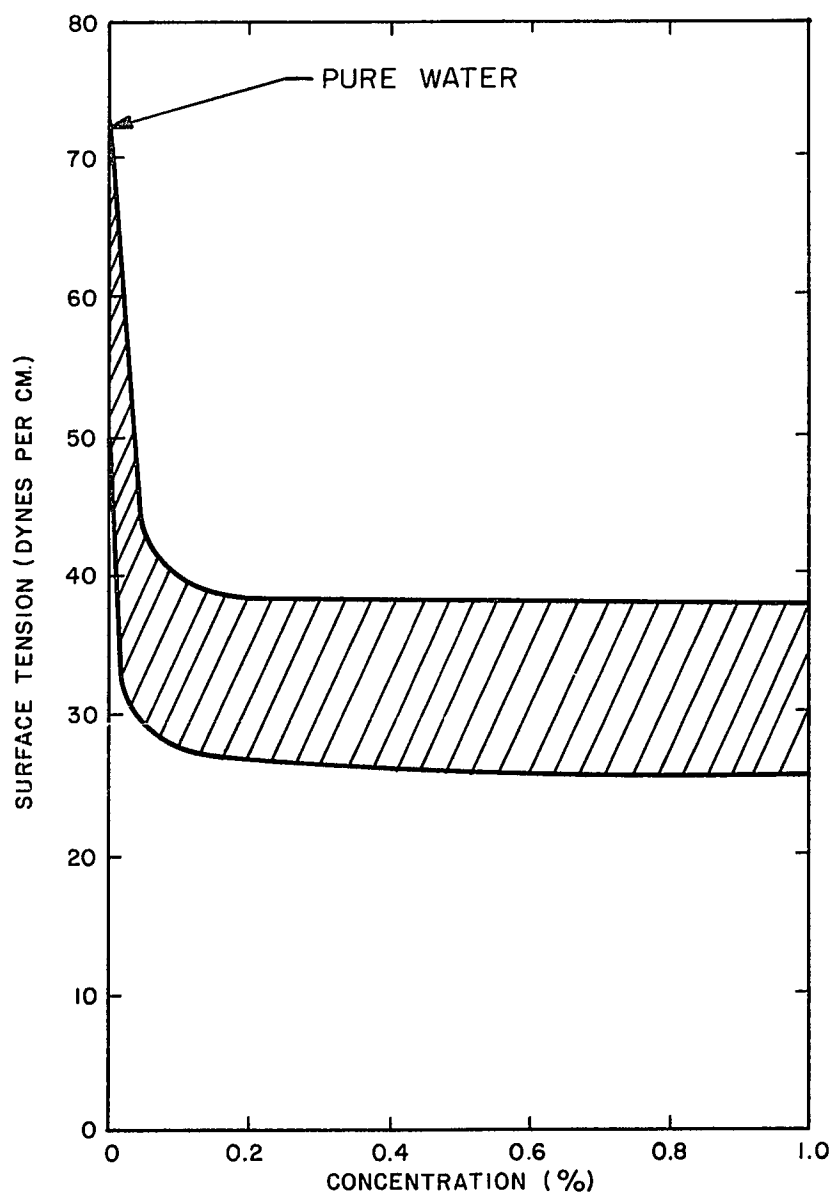


FIGURE 48. SURFACE TENSION VALUES FOR THE MAJORITY OF SURFACE - ACTIVE AGENTS FAIL WITHIN SHADED AREA ON THE GRAPH

surface wetting figures. First, it can be seen that the initial contact angle decreases as the concentration of the surfactant increases. Next, the contact angle with water as the wetting agent remains constant over the observation period when it was applied to all non-groundwood papers. Also, the contact angles are markedly lowered with time when any surfactant is used as the wetting agent. Furthermore, many individual surface wetting curves exhibit irregular patterns consisting of starts and jerks as the contact angles change with time. It appears that this behavior is caused by product irregularities and the simultaneous capillary wetting occurring while the surface is wetted. As the surface drop disappears, capillary wetting is proceeding along the paper surface and, also, internally in the paper structure. The changes in the equilibrium states, both externally and internally, account for the nature of these irregular wetting curves.

Comparing Figure 16 to Figures 17 and 18 shows that the contact angles decreased with increasing concentrations of the surfactant and the curves are higher for the starch sized groundwood than for the others.

From a comparison of the transient contact angles between the wet-strength and regular-strength kraft shipping sacks shown in Figures 19 and 20, one can see that the wet-strength paper is more susceptible to surface wetting than the sample without this additive. When the various concentrations of the surfactant were used to surface wet the samples, major differences can be seen between the

curves. The initial contact angle values for the regular-strength kraft paper are higher than those of the wet-strength one.

Comparing Figures 22 to 24 enables one to determine the effects of wetting due to basis weights and also a wet-strength additive. From Figures 22 and 24 one can see that the heavier, thicker paper takes longer to reach equilibrium wetting than the lighter, thinner one. Similarly, by contrasting Figure 23 with either of these other figures, one can see that the wet-strength additive results in higher curves indicating that this paper is more resistant to wetting than either of the non-treated sacks.

Differences between bleached and unbleached shipping sacks of the same basis weights can be seen from Figures 19 and 24. The bleaching process produces a form of surface wetting resistance which is not present in the unbleached sack using the quaternary ammonium derivative surfactant. Using this same syndet Figures 21 and 25 show the pronounced affinity of the wax coating as the drop spreads over the surface compared to uncoated bond sample. From these figures it can be seen that there is a higher angle of contact, and hence greater water resistance, on the wax-coated paper than on the uncoated one. For any of the surfactant concentrations, the resulting curves of the foodboard exhibit low initial contact angles which steadily declined with time.

The transient contact angles using the alkyl aryl sulfonate on some of the paper samples are shown on Figures 26 to 30. A comparison of Figures 26 and 27 shows differences between the bleached wet-

strength and regular-strength shipping sacks. The results are similar to those obtained for the different concentrations of the cationic surfactant. This indicates that the chemical composition of the additives is more reactive to either of these surfactants, regardless of charge, than on the untreated paper. So that, in both instances, the wet-strength paper exhibited faster surface wetting than the regular-strength shipping sack.

The differences between the behavior of the samples shown in Figures 27 and 28, which both had wet-strength additives, indicate that the additives are not identical. The one applied to the bleached sack resulted in accelerated wetting when either of the charged surfactants was used compared to its untreated counterpart. The additive used on the unbleached sack retarded the wetting of both surfactants when compared to its untreated counterpart.

Comparing Figure 28 with Figure 30 shows that the lighter 40# sample surface wets faster than the heavier 60# sack. This is also what occurred with the cationic surfactant. The wet-strength chemical shows again a greater wetting resistance than either of these other untreated samples, Figure 29. This was also shown when the cationic surfactant was used.

#### Capillary Penetration

The internal wetting process in porous material depends upon the physical and chemical properties of the paper and the capillary wetting power of the wetting liquid. The important physical properties for this process include the size and distribution of the capil-

laries and openings between the fibers. The chemical properties depend upon the paper manufacturing processes which, besides the cellulose fiber, include the chemicals and additives used to form the finished product. By subjecting all the samples to the various liquids, the different paper properties can be determined to isolate the important factors which govern this stage of wetting.

Comparing Figures 31 and 32, for the quaternary ammonium derivative surfactant, or Figures 33 and 34, for the capillary penetration of the alkyl aryl sulfonate surfactant, shows that in both instances the catalog wets faster than the textweb. Similar results were obtained for surface wetting of these papers. Because the capillary wetting as expressed by Lucas and Washburn<sup>(55)</sup> is a product of  $\gamma_{LG} \cos \theta$ , the maximum wetting power should be obtained with water and a low contact angle. By using a surface-active agent, the surface tension and, also, the contact angle are reduced resulting in a lower product. This accounts for the reduced penetration with either surfactant compared with that of water.

An examination of Table 24, obtained for the internally rosin sized catalog paper, shows consistently lower factors for all cationic liquids than that calculated for water. The values for the different anionic surfactant concentrations are reasonably close, both above and below, to those of water. The use of cationic syndets shows greater chemical affinity with the rosin sizing resulting in fiber swelling, than that obtained with the anionic surfactant which behaved similarly to pure water.

Similarly Table 25 shows that these values also fall into two groups which indicate different chemical reactions caused by the clay additive. Where the proportionality factors were fairly close for the anionic liquids and water in the rosin sized catalog, the additional clay additive results in changes of the capillary structure using the anionic liquid compared to that of water.

An examination of these tables indicates that the chemical behavior of the surfactants can appreciably alter the penetration because of the reactions occurring between the surfactants and the paper additives. It is assumed that the theoretical expression for capillary wetting is equal to  $\gamma_{LG} \cdot \cos \theta$ .

The fact that none of the bleached kraft papers showed any capillary penetration suggests that excessive swelling occurred as the cationic surfactant was absorbed on the fibers which restricted the pore spaces. The bleaching process has been discussed previously, but some of the major points will be restated to explain the different ionic strengths resulting on the sites of bleached and unbleached fibers. Chlorination, regardless of which chemicals are used, either chlorine or chlorine dioxide, is intended to remove the lignin and other non-carbohydrate components from the cellulose. The chloro-lignin compounds are then extracted from the cellulose by washing the pulp with very alkaline hypochlorite. These processes alter and reduce the surface charge on the cellulose fibers which weakens the resulting bleached paper strength.<sup>(75)</sup>

The differences in the surface charge of bleached and unbleached



fibers are also important to the preparation of the sheet formation when polymers are added to enhance floc formation, improve pulp drainage, or improve strength of the finished product, or when dry-strength resins are used to increase fiber bonding. The differences in the surface charge are important in this work because of the fiber's influence to retard or enhance capillary wetting.<sup>(76)</sup> Figure 49 shows the bonding of the cationic surfactant to bleached and unbleached fibers. The bleached fibers on the left have few anionic sites and, while the cationic surfactant is adsorbed on the cellulose, the bonding is weak. The strong anionic charge of the unbleached fibers, shown on the right, is the result of the lignin, hemicellulose, and the cellulose components. These unbleached fibers provide many negative sites for the cationic surfactant attachments.<sup>(77)</sup>

The bonding of the cationic surfactant on all the unbleached kraft papers resulted in appreciable fiber swelling so that capillary movement of the liquid was restricted in the passageways. The bonding of the cationic surfactant on the bleached kraft shipping sacks, on the other hand, was not as strong so that capillary wetting occurred.

Previously with the quaternary ammonium derivative surfactant, only the bleached papers showed any appreciable capillary penetration due to its reduced negative surface fiber charge. With that surfactant the high negatively charged sites on the unbleached fibers were causing great attractions, Figure 49. This resulted in swollen unbleached fibers that resisted capillary movement of the liquid.

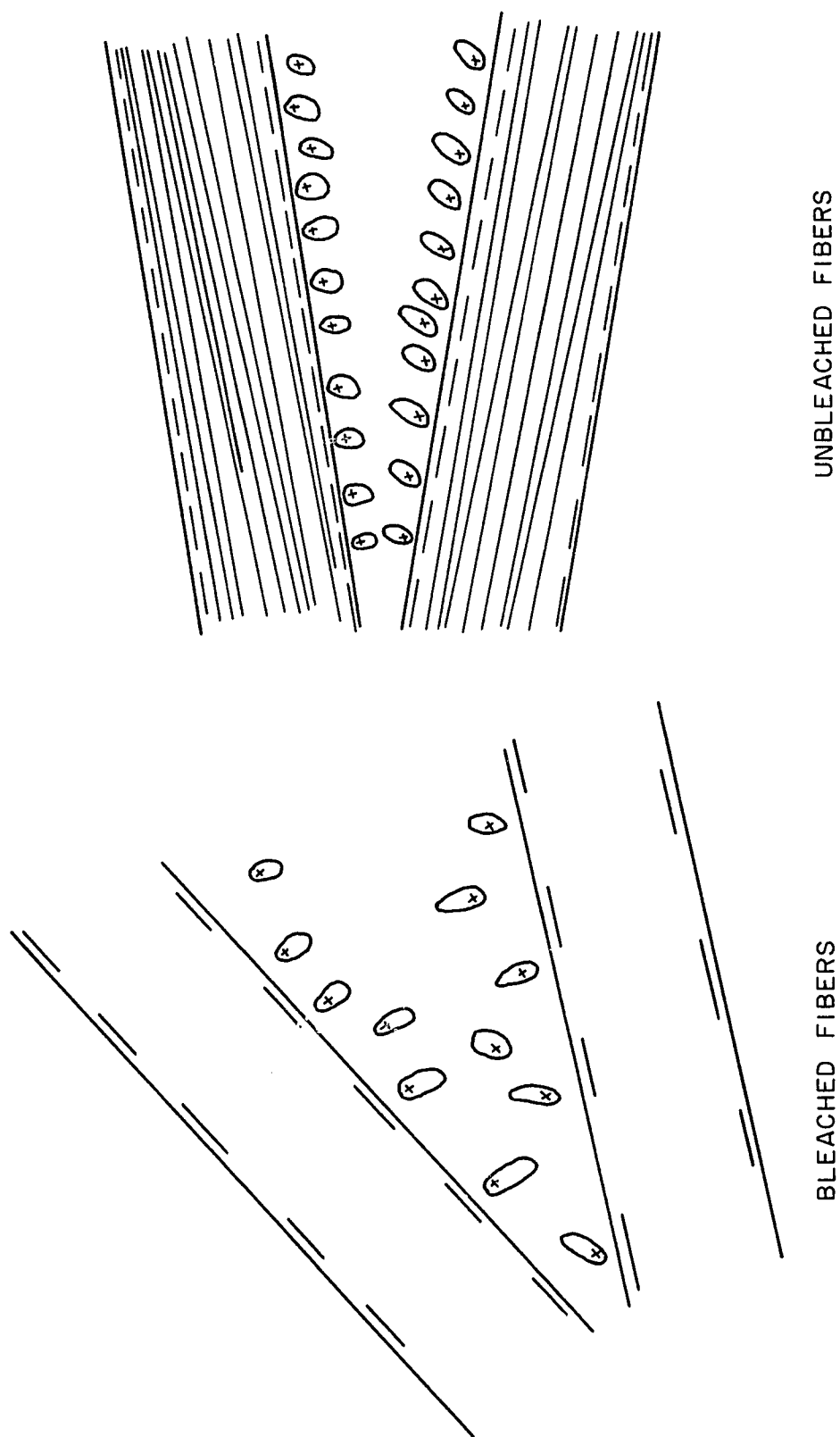


FIGURE 49. BONDING OF CATIONIC SURFACTANT ON BLEACHED AND UNBLEACHED FIBERS

The results with the anionic surfactant are quite the opposite due to the different charge of the surfactant. In this instance the negatively charged hydrophobic end of the surfactant, together with the appreciably negative charge on the unbleached fiber sites, due to lignin as well as the cellulose present, results in little attraction so that this liquid can wet throughout the porous structure. No bleached shipping sacks exhibited any capillary movement with any of the various anionic surfactant concentrations because of the reduced level of the surface charge on their fibers. By comparing the curves in Figure 36, it is apparent that a higher rate of capillary wetting and depth of penetration at any time occurs for the thicker, heavier paper. It should be noted that the lighter, thinner paper surface wetted faster than the bulkier one as the liquid drops spread over the surfaces. The 50#, wet-strength paper was less active than the other unbleached ones when surface wetted, but from this figure it can be seen that the additive only delays capillary wetting initially and that it soon proceeds quite rapidly.

#### Thermodynamic Properties

From the laboratory bench scale wetting determinations on the individual paper samples, it is possible to draw some observations relating the thermodynamic properties to the wetting processes.

Several features are noteworthy about Tables 26 to 29. When the tables are arranged in the order of increasing surfactant concentration, the contact angles,  $\theta$ , are in a decreasing order and the surface wetting powers, or spreading coefficients,  $W_s$ , are in an increasing order.

Furthermore, with the exception of the catalog and textweb ground-woods, all the capillary wetting powers, also called the adhesion tension,  $\gamma_{LG} \cos \theta$ , are also arranged in an increasing order. The interfacial affinities, or work of adhesion,  $\gamma_{LG}(1 + \cos \theta)$ , all have minimums at the most dilute surfactant concentration.

It has already been shown theoretically and experimentally demonstrated that the surface wetting of the paper samples is always improved, whereas the capillary wetting may or may not be improved by using syndets. The surfactant by lowering the surface tension and the contact angle will always reduce the product  $\gamma_{LG}(\cos \theta - 1)$  for surface wetting expression. This, however, is not necessarily advantageous to the capillary wetting which is proportional to  $\gamma_{LG} \cos \theta$ ; but, it can be. Under certain conditions the contact angle can be reduced to such an extent that the expression will more than compensate for the reduction of the surface tension.

The condition for improved capillary wetting is that the contact angle between the solid-water interface must be relatively high. For values above this contact angle the capillary wetting will be improved with the surface-active agent; otherwise, it will not be improved. This value can be calculated from the condition for improving capillary wetting

$$\gamma_{SAGG} \cos \theta_{SAA} > \gamma_W \cos \theta_W$$

where  $\gamma_{SAGG}$  = surface tension of syndet,  $\theta_{SAA}$  = contact angle with syndet,  $\gamma_W$  = surface tension of water, and  $\theta_W$  = the contact angle with water.

The surface tension for the quaternary ammonium derivative surfactant was determined to be 35 dynes/cm at high concentrations. At these levels the efficiency of the surfactant was great enough so that the contact angles reduced to about zero for all the paper samples. From the above equation one can see that the contact angle of the water-solid interface must be above  $60.9^\circ$ .

Based upon this value and the results in the tables from our paper samples, it can be seen that the surface-active agent improved the capillary wetting of only the hydrophobic papers but decreased the wetting of the hydrophilic samples. The capillary rate of penetration of the most hydrophilic catalog and textweb groundwoods has been mentioned previously. Based upon the general Lucas-Washburn<sup>(55)</sup> equation for capillary penetration, where  $L^2 = K \chi_{LG} T$ , the plots of  $L^2$  versus  $T$  should be linear. Furthermore, the slopes of these curves should be high initially and decrease as the surface tension decreases.<sup>(78)</sup> Figure 37 which has been plotted for both of these paper samples shows that these curves give a good fit to a straight-line relationship. Also, the slopes for both papers decrease when the surfactant is used instead of the water as the wetting liquid. It has been assumed that the viscosity factors, included in the  $K$  value, is relatively constant at low surfactant concentrations.<sup>(79)</sup>

In general, only very dilute solutions of the surface-active agents were found to be useful in the quiescent recovery tests in establishing workable detention times and determining desirable recovery groups. Except for the hydrophilic groundwood samples, all

other papers samples were precluded from capillary wetting at these low surfactant levels. The contact angles had not been lowered sufficiently for the capillary penetration of the hydrophobic papers to proceed.<sup>(80)</sup> This can be seen in the values for the capillary wetting power in the tables.

Even at low concentrations of surfactant, the surface wetting is drastically increased. This is confirmed for all the paper samples in the tables where all the values for the surface wetting power,  $\gamma_{LG}(\cos \theta - 1)$ , decrease numerically as the surfactant levels increased.

Because the surface wetting is primarily responsible for the wetting and sinking under quiescent conditions, one would expect some relationship between these values and the detention times. Figures 38 to 41 give the curves  $\gamma_{LG}(\cos - 1)$  versus detention time for all the paper samples in their respective group. It is worth noting that with only one exception, all bleached papers plot as straight lines.

The exception was the heavy container foodboard which had been wax coated. Additional studies were performed to determine its wetting characteristics which caused this behavior. It was found that the amount of wax applied to this paper was sufficient to appreciably alter all results of detention time determinations. Because of the resulting buoyancy due to the large amount of wax applied to the cellulose fibers, even after shreading, all fibers were found to remain floating on water and to resist wetting indefinitely. The individual fibers remained on the water surface for several months because of this large amount of additive. When the faces of this sample were

separated and added to dilute surfactant concentrations, both faces of the chip wetted more rapidly than that observed for its sulfite counterpart, the bond paper sample. However, with the faces intact, this sample was consistently the most resistant to wetting. Evidently the surfactant could easily attach itself to the wax molecules but was prevented, perhaps by its size, from penetrating the surface to the internal pores to a large extent. With the sides separated, this was clearly not the case. The face was easily wetted on both sides by the surfactant molecules and the chips rapidly sank.

The non-linear curves, for all the unbleached kraft samples, clearly indicate that surface wetting alone is not the only important process which affects the detention times. The important charge differences on the fiber surfaces between bleached and unbleached products have already been mentioned and observed during the capillary determinations.<sup>(76)</sup> Here, once again, the highly negative charge on the unbleached fibers can be seen to be very reactive with the positively charged surfactant.

From Figures 38 to 40, it is obviously possible to estimate the detention times of the bleached paper groups by observing the contact angle. For the unbleached papers, a less accurate estimate can be made from Figure 41. The implication of the observed regularities is that, for dilute surfactant concentrations, no other process is as important as the surface spreading which displaces the trapped air in the fibers and results in paper sinking.

Using the assumption made earlier that  $\gamma_{SG} = 0$ , the spreading

term reduces to the simple relation

$$W_S = W_A - W_C = \gamma_{LG} (\cos \theta - 1)$$

Since this has been shown to be a linear function of the detention time,  $T$ , it becomes easy to find the required relations by determining the equations of the straight lines in the form

$$W_S = \gamma_{LG} (\cos \theta - 1) = aT + b$$

The coefficients  $a$  and  $b$  are given in Table 32. The intercept,  $b$ , values directly give the critical spreading coefficients where instantaneous wetting and sinking will occur. The slopes, or  $a$  values, indicate the relative degree of wetting that occurs for the individual paper groups. The greater the value, the more rapid will be the paper wetting due to its specific sizing additives and manufacturing production.

Besides being able to predict the detention times for the separate papers, these values can be used to make comparisons within our paper samples to determine the important wetting parameters. The steepness of the slopes indicate that all bleached papers tend to wet faster than the unbleached fibers. This is also explained by the differences in the surface charges for these papers.<sup>(76)</sup> Furthermore, the slopes and intercepts show that within the bleached papers the most rapid wetting occurs in the order groundwoods, sulfites, kraft. The wet-strength additive may or may not increase the rate of wetting over its regular strength counterpart depending upon its specific chemical composition. The additive used in the bleached sample has a steeper slope than the regular-strength sack; but the one used in the manufacture of the unbleached paper retarded surfactant wet-



| <u>PAPER GROUPS</u>     | <u>a</u> | <u>b</u> |
|-------------------------|----------|----------|
| Groundwoods             | -1.09    | -12.9    |
| Kraft, regular-strength | -0.20    | -20.5    |
| Kraft, wet-strength     | -0.28    | -18.8    |
| Sulfite                 | -0.29    | -20.2    |

Values computed by least-square fit.

TABLE 32. THE SPREADING COEFFICIENT AS A FUNCTION OF DETENTION TIME IN THE FORM

$$W_S = W_A - W_C = \gamma_{LG}(\cos \theta - 1) = aT + b$$

ting. The relative steepness of the slopes for the groundwood papers shows that the most rapid wetting, due to sizing and coating additives, occurs in the order of clay coating, rosin sizing, and starch sizing. The results also indicate that lighter thinner papers are more easily penetrated than thicker, heavier ones as the liquid moves through the pores. (81)

#### PILOT PLANT SYSTEM

Because the unmixed quiescent recovery results were so promising, it was decided that a larger mixed recovery demonstration system, based upon the preferential wetting principle, should be developed. The quiescent recovery results were all obtained from floating chips allowed only to wet on the face directly in contact with the wetting liquid. Paper overlapping was purposely kept to a minimum so that all chips had equal access to fully wet on the liquid surface. There was no competition between the individual chips for this desirable liquid interface which lowered their detention times. But, because the loading rates were insignificant, this unmixed system would have severely limited practical applications. The results did, however, serve as useful guidelines for determining possible desirable separations that could be obtained with specific surfactants.

The parameters measured under this dynamic system included the paper shape effects on detention times and settling rates, loading rates, power requirements, and the factors influencing the batch wetting process.

### Paper Shape Effects

Table 30 and Figure 42 indicate that shape is not an important factor on the detention times of the recovery process. The results are similar to those obtained when only one-inch square chips were used to determine detention times. In addition to recording and plotting the recovery results, the individual paper chips were visually examined after they had wetted enough to begin sinking and, also, after they had been on the tank bottom for some time. It was found that the wetted papers showed distinct dark liquid areas which appeared throughout the surfaces of all papers regardless of shape. The sheet wetting occurred as the liquid transuded through the pores perpendicular to the paper surface. Figure 50 shows a photograph of the transudation on square and circular paper samples. The two samples on the left have not been subjected to liquid wetting and show uniform tones. The samples on the right show darkened areas of blotchiness where the black background can easily be seen through the paper. It was found that the degree of blotchiness increased, as well as the total dark areas, with the length of time the papers had been in contact with the wetting liquid. As the liquid penetrates the paper, enough air is displaced to result in paper sinking but the process continues even while the papers are on the tank bottom. This clearly shows that regardless of shape the liquid penetration occurs primarily through the surface of the paper.

The sinking behaviors of the different shapes were observed and photographed through the plexiglass tank wall. Figure 51 shows

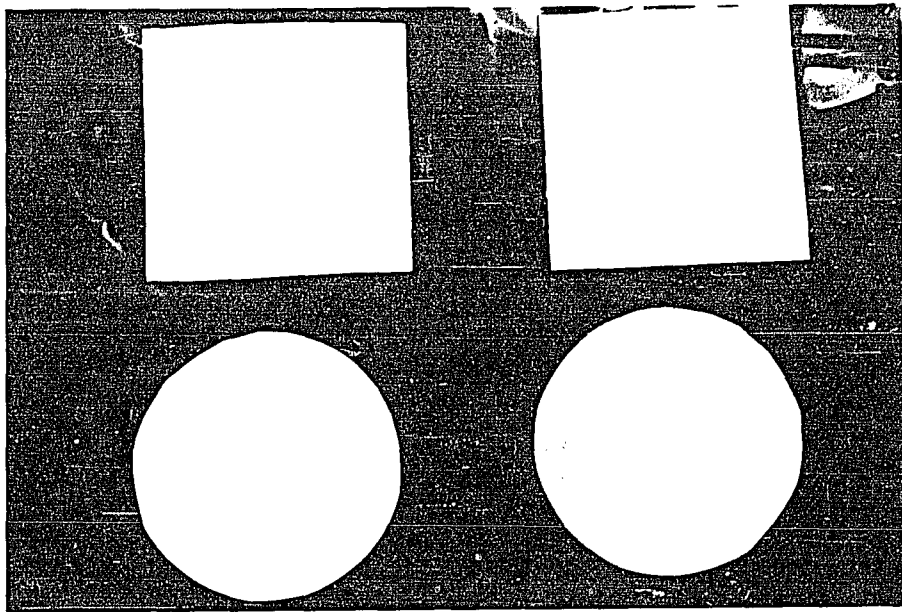


FIGURE 50. PHOTOGRAPH SHOWING UNIFORM WHITE TONE ON DRY PAPER CHIPS, ON THE LEFT; AND, DARKENED AREAS WHERE LIQUID HAS PENETRATED THROUGH THE SURFACES, ON THE RIGHT

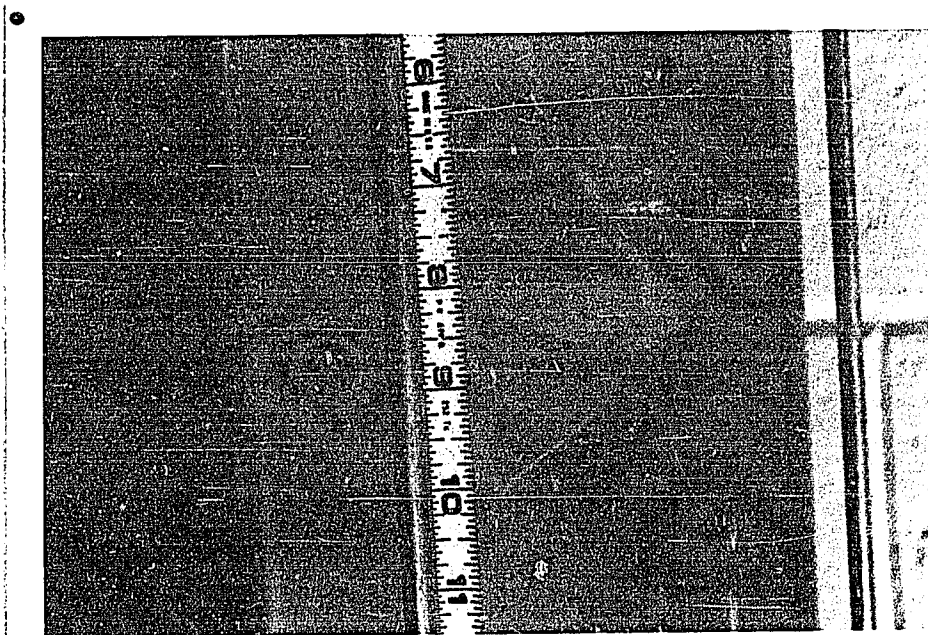


FIGURE 51. PHOTOGRAPH OF A CIRCULAR-SHAPED PAPER CHIP IN A SETTLING COLUMN

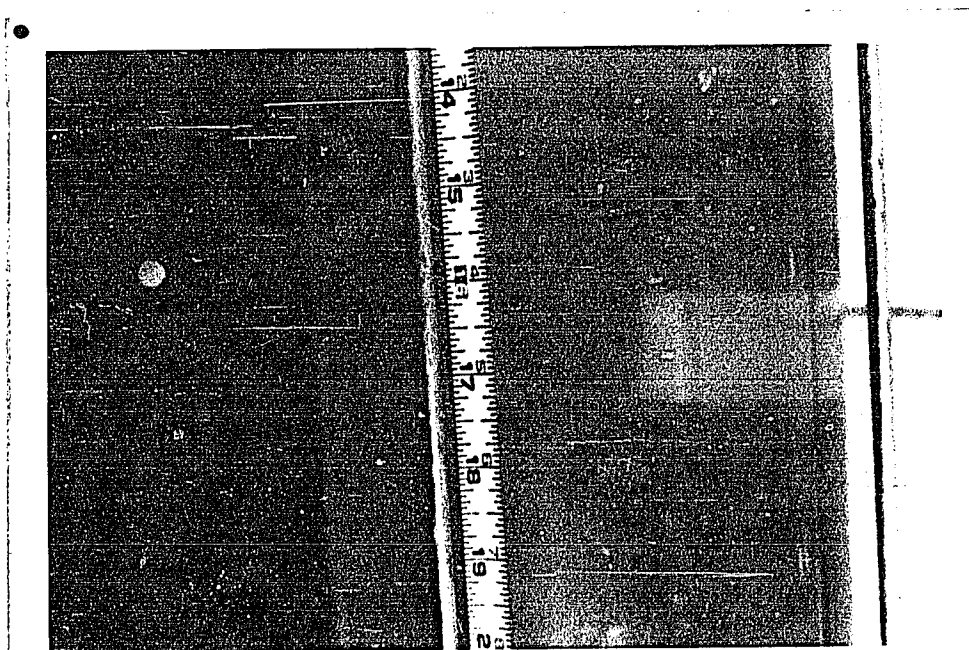


FIGURE 52. PHOTOGRAPH OF A SQUARE-SHAPED PAPER CHIP IN A SETTLING COLUMN

a circular paper chip falling in the column. This shape frequently descended with the sheet surface remaining parallel to the liquid surface. This chip settled with a gentle rocking and rotating motion throughout the entire column depth. Figure 52 shows a photograph of a square shaped paper chip during the settling process. These shapes did not oscillate as did the circular ones, but steadily descended to the bottom in a direct path. While the circular shaped chips had slower settling rates than the square ones, both shapes sank directly to the tank bottom while dislodging attached air bubbles which increased the rate of descent.

#### Loading Rates and Power Requirements

With the use of a large tank and a mixer, it was felt that many operational and design parameters could be established for the further development of a pilot plant operation. The factors which were investigated using this demonstration system included the following:

1. mixing agitation studying the effects of type and methods of application,
2. detention times and recovery using mixing on individual samples,
3. operating performances and loading rates for batch systems,
- and 4. power requirements.

The recovery curves from Figure 45 clearly show that the detention time is dramatically reduced as the mixing speed is increased. The detention time at an operating speed of 62 rpm was less than one-half of the detention time required for an unmixed system. All the curves from Figures 45 and 46 show that at low loadings the detention times are all reduced when mixing is employed rather than quiescent

conditions. Furthermore, any increase in the mixing speed results in further detention time reductions.

It was possible to determine the loading rates because this tank was much larger than the ones used to study quiescent paper recovery. Besides having a greater surface area, the increased volume, with mixing action, served to continuously separate, scatter, and contain the paper chips. In all the quiescent recovery studies, the paper chips were contained solely on the liquid surface where they floated. In this system, the tank volume also served as a storage reservoir while the mixing provided a means to introduce new paper chips to the surface.

The operation of the tank resulted in many interesting observations. Figure 53 shows a view of the top of the tank after a batch load of paper was applied. It indicates a great deal of overlapping and sandwiching between all the chips. This shows that the chips that are on top of the others are currently being hindered from wetting on the liquid surface. The mixing agitation provided an excellent opportunity for all papers to become wetted by the liquid.

The wetting of the individual chips near the liquid surface can be seen in Figure 54. This photograph clearly shows that the majority of all the paper chips was below the liquid surface. While the chips on the surface were all laying horizontally on the liquid, those below were pulled beneath the overlaying ones. The action of the mixer drew them down so that wetting on both sides of the chips could occur.

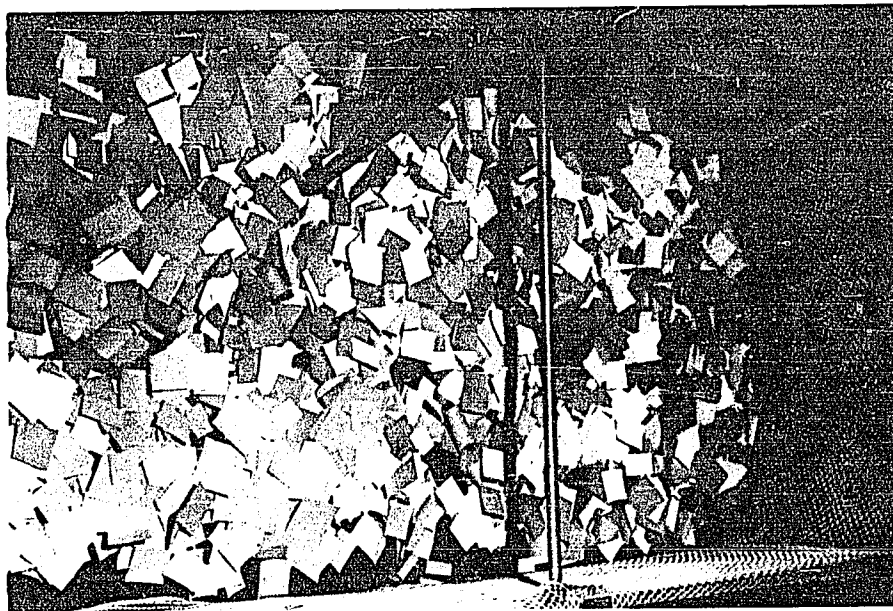


FIGURE 53. TANK DURING BATCH LOADING SHOWING SCATTERING OF PAPER CHIPS ON LIQUID SURFACE





FIGURE 54. WETTING OF PAPER CHIPS BENEATH THE LIQUID SURFACE  
IN PAPER RECOVERY PROCESS WITH THE BATCH PLANT  
SYSTEM



FIGURE 55. SCATTERING AND MIXING THROUGH THE TANK IN PAPER  
RECOVERY PROCESS WITH THE BATCH PLANT SYSTEM

Another important observation was made which related to the operation of this system. Figure 55 shows the high degree of scattering that occurred throughout the tank. Vortexes that resulted around the propeller caused frequent flushing where large amounts of papers were sucked down from the surface so they could be dispersed throughout the entire tank. This action constantly replenished the supply of papers so that new chips were always being introduced at or near the liquid surface. This type of mixing occurred for all loadings until a sufficiently large amount of papers was added to the tank. The large number of chips and their total weight caused severe sandwiching to occur on the surface so that this type of flushing action, which mixed and replenished the papers at the surface, was hindered.

An optimum for this degree of recovery at the specific mixer speed and surfactant concentration level can be seen to occur near the total batch load of 750 grams. For this quantity of papers 170 minutes of detention time were necessary to achieve the desired recovery level. These loading rates were determined to be  $1.74 \text{ lb/ft}^2/\text{day}$  based on the available tank surface area or  $103.9 \text{ lb/1000 gal/day}$  based on the tank volume. The electrical power requirements were determined to be 0.412 kilowatt-hours to treat one pound. The optimum loading rate was close to 40 times higher than that which could be achieved for an unmixed separation system.

At higher batch loadings than the optimum, the additional mass and number of chips caused severe hindering of those chips near the liquid surface so that many of them were prevented from being ade-

quately mixed by the propeller. As a result, many of the papers above the liquid surface were not given an opportunity to effectively move throughout the tank by the propeller action and remained relatively stagnant in the conglomeration of papers.

The operating curves shown in Figure 47 indicate that as the loading rates were increased, longer detention times were required to achieve the same level of recovery. It should be noted that these detention times are longer under this batch form of loading than when the bleached samples were used alone. Apparently the large number of unbleached paper chips are interfering with the ability of the bleached chips to come in contact with the wetting liquid. But even though the detention times have been lengthened, the through-put of the system has increased significantly.

## VI CONCLUSIONS

Based on this investigation dealing with a paper recycling process using selective wettability to recover similar secondary fibers, the following conclusions can be made:

1. A separation process has been developed which recovers similar paper grades from a mixed stock by selective wettability. This method can be used advantageously to achieve higher percentages of secondary fiber recovery resulting in a savings of labor and virgin timber and a reduction in the solid waste problem.
2. A pilot plant was developed that recovered selected grades from a mixture which had been batch loaded. The viability for commercial applications has been shown through loading rates and power requirements that were generated.
3. It was determined that agitation dramatically reduced the detention times and increased the through-put which could be achieved under quiescent settling conditions. Gentle slow-speed mixing was found to be preferable over violent high speeds due to fiber separation and agglomeration.
4. It has been found that most paper additives tend to retard water wetting which results in paper floating for prolonged periods

of time before they begin to wet and sink. If water is used to recover and separate papers, extremely long detention times are required to achieve desirable groups. Consequently, water separation for recovering secondary fibers would have severely limiting industrial applications.

5. It has been shown that surface-active agents can be used to significantly lower detention times and can be used advantageously to separate specific paper groups from a mixed stock. Low concentrations must be used since at high concentrations all papers wet too rapidly to allow for practical separations.

6. Since surfactants currently have many applications in recycling processes at high concentration levels, it is believed that the low concentrations required in this process will not adversely influence the fiber properties.

7. The wettability of the papers was determined for both the surface spreading and capillary penetration processes to isolate differences between the samples. The detention times for the bleached papers were found to be proportional to the surface spreading coefficients so that predictions for their recovery can be made for cationic surfactants. Several TAPPI sizing tests for wetting-resistant papers support this penetration mechanism. The fiber surface charges were found to be significant when separating bleached from unbleached papers.

8. It was shown that the sizes and shapes of paper samples do not have any appreciable effects on the resulting detention times. The wetting liquid transduces perpendicularly through the paper sur-

face displacing air from the pores while the sample remains floating. When the specific gravity of the paper eventually exceeds that of the liquid, the paper sinks directly to the tank bottom while continuing to absorb more liquid.

9. Based on observations, it was found that all groundwood fibers tend to wet faster than chemically produced papers. Any ionic or non-ionic surfactant in a low concentration can be effectively used to recover them from other mixed grades in a reasonable time period under static, quiescent conditions.

10. Cationic surfactants, in low concentrations, were used to effectively separate, by lowering detention times, bleached from unbleached papers in a reasonable time.

11. Anionic surfactants, in low concentrations, were shown to effectively separate, by lowering detention times, unbleached kraft paper from bleached kraft paper in a reasonable time.

12. Non-ionic surfactants were found to exhibit non-specific wetting behaviors on the various groups of papers, so that they would be of limited use in this separation process.

While this country continues to waste the majority of its paper fiber, there are many people who feel that this loss of a reuseable resource should not, and need not, be tolerated. Besides the direct cost of additional billions of dollars worth of virgin paper needed to replenish those discarded and lost into the solid waste stream, additional factors which are increasing the interest in reclaimed fiber include conservation of our timber forests, energy depletion, and pollution abatement. It is generally agreed that increasing our

paper recycling levels will enhance our efforts in all these vital areas. It is hoped that this research will help in achieving some of these goals.

## VII RECOMMENDATIONS

While this study has developed a new paper recycling process based on selective wettability using surfactants, it is recognized that there are several areas which were not investigated because they were outside the scope and intent of this work. To assist in further developing a viable commercial scale system based on this wetting process, several recommendations can be made.

For instance, while the paper samples were carefully selected to represent the bulk of papers that could be encountered in a commercial waste stream, they intentionally did not include any dyed, typed, or printed samples. It is suggested that these papers, as well as other common commercial grades, such as tissues, magazines, converted grades, and board, be used in additional investigative work. Because this process could be applied on a commercial scale to treat, recover, and recycle high-grade stock, mixed papers from office buildings, institutions, and similar sources should be used to measure the efficiency in a commercial prototype plant.

The pilot plant used in this study to effectively recover similar paper grades was operated under a batch loading operation. There



are several recommendations which can be made to measure the efficiencies of other possible systems. Comparisons could be made between this settling tank operation and one that was continuously operated. This type of tank could have a paper shreader and hopper at the head-end to provide a continuous paper source as well as skimmers and bottom scrapers to provide continuous paper removal. Different agitators could be used such as mechanical and pneumatic types with various arrangements. A series of tanks could also be used to achieve additional recovery groups from a primary stock.

It is recommended that attention be focused in other areas which might improve the operations of a commercial system. Some of these items to be studied could include the temperature effects of the process liquid, contaminant effects such as plastics and metals found in typical wastepaper stock, and the recovery effects using mixed ionic surfactants. While several new methods are capable of separating and recovering wastepaper from mixed wastes, none of these processes successfully upgrades the fiber properties. It is suggested that the papers generated from the Balck Clawson Fiberclaim process, the Stanford Research Institute's air classifier, or another recovery system be introduced into this wet-separation process to upgrade the reclaimed material.

Several recovery systems could be designed to treat and recover mixed paper from a mixed stock. For a given paper mixture the important variables which determine possible recovery groups include the surfactant, its concentration, and the order of the wetting sequences. As an aid in designing an entire sequence of recovery operations to

make several separations, an example is presented using the paper grades used in this investigation. A flow diagram of recovery operations to achieve high-grade fiber is shown on Figure 56. The proposed sequence of operations for this system is described in Table 33.

Before the mixed wastepapers are subjected to any wetting, it is suggested that pretreatment operations be used to remove heavy contaminants and to mix and scatter the incoming material. A fan shredder can be used to break up the material initially. The papers could then be subjected to an air-blower cyclone to mix them while segregating out heavy material such as paper clips, staples, and grit. The high specific gravity items collected during this stage would reduce the amount of contaminants that currently must be removed during the secondary pulping stages.

Three settling detention tanks are proposed to treat and recover the high-grade pulp substitutes from the mixed papers. These tanks can be provided with scrapping device, to collect the recovered papers in a sump where they can be withdrawn, and with a skimmer, to transfer floating papers to another settling tank or directly to a process hopper for secondary pulping. In addition to these mechanical collectors, the tanks should be equipped with paddle flocculators, mixing impellers, or air diffusers to provide gentle agitation and mixing of the papers throughout the tank. Detectors could be used to check and monitor the concentration of the surfactant in the tank. If the surfactant level was low, an automatic feeder could be used to replenish the stock. A liquid return line could be used to help equalize the liquid constitu-

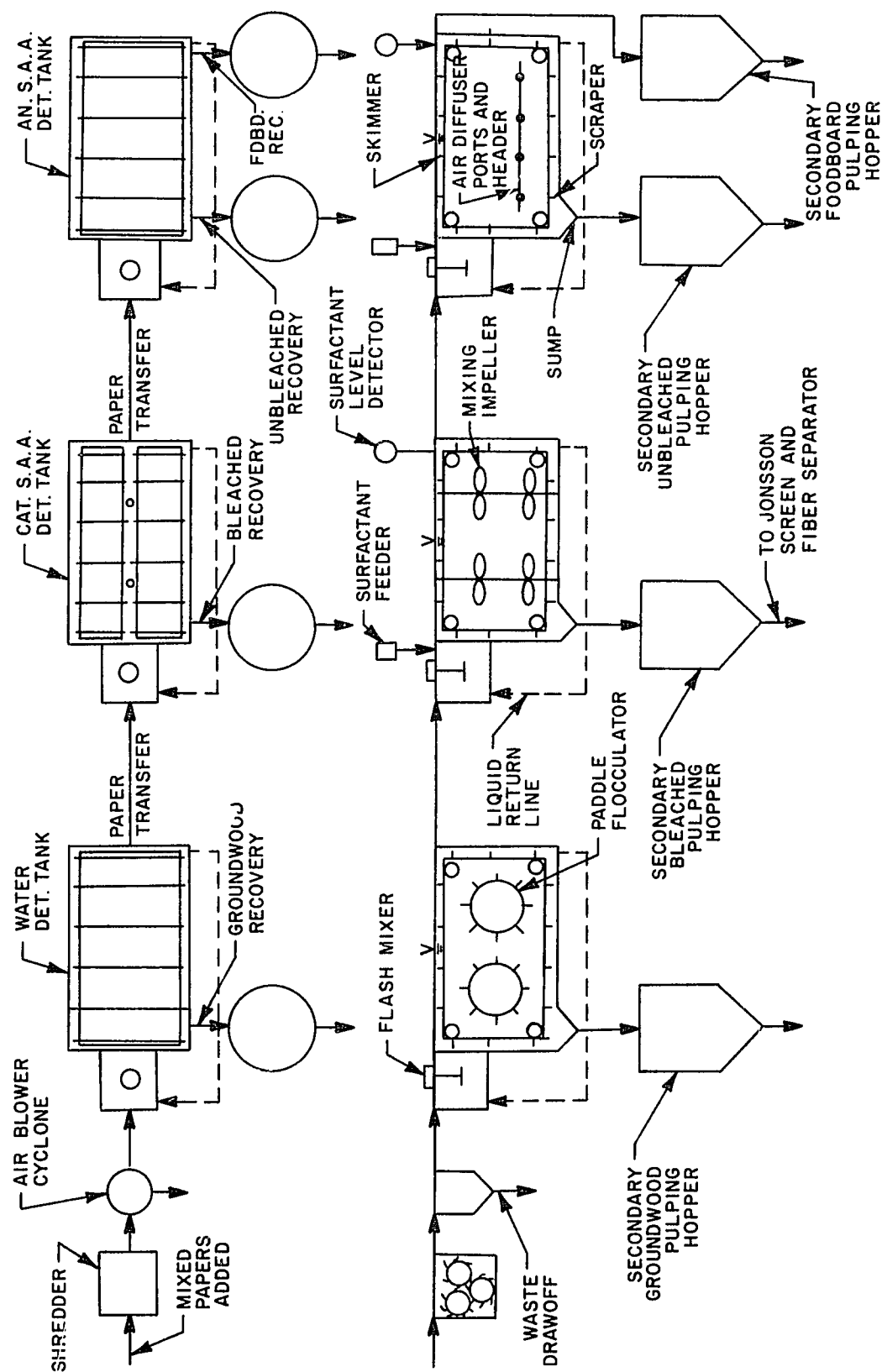


FIGURE 56. FLOW DIAGRAM OF RECOVERY OPERATIONS TO ACHIEVE HIGH-GRADE FIBER FROM MIXED PAPERS

Sequence of Operations

Comments

- |   |   |   |
|---|---|---|
| 1 | Introduce mixture into tank containing water (30 tons/day batch loaded every 3 hours)       | Groundwoods will settle leaving remaining papers floating             |
|   | a. Remove groundwoods from tank using bottom scraper (30 min. det. time; .83 tons)          | Groundwoods have been recovered for recycling                         |
|   | b. Remove all floating papers using skimmer for additional treatment                        |   |
| 2 | Transfer floating papers to tank containing cationic surfactant (2.92 tons transferred)     | Bleached uncoated fibers will settle from unbleached papers           |
|   | a. Remove bond papers from tank using bottom scraper (1 hr. det. time; .33 tons)            | Bleached bond papers have been recovered for recycling                |
|   | b. Remove kraft shipping sacks after additional detention time ( 3 hr. det. time; .73 tons) | Bleached kraft sacks have been recovered for recycling                |
|   | c. Remove all floating papers using skimmer for additional treatment                        |   |
| 3 | Transfer floating papers to tank containing anionic surfactant (1.86 tons transferred)      | Unbleached kraft sacks will settle from coated bleached               |
|   | a. Remove light-weight kraft sacks from tank using bottom scraper (1 hr.; .29 tons)         | Light-weight unbleached kraft sacks have been recovered for recycling |
|   | b. Remove heavy-weight kraft sacks after additional detention time (2 hr.; .80 tons)        | Heavy-weight unbleached kraft sacks have been recovered for recycling |
|   | c. Remove all floating papers using skimmer (.77 tons transferred)                          | Coated cup-sidewalls have been recovered for recycling                |

TABLE 33. PROPOSED SEQUENCE OF RECOVERY OPERATIONS TO ACHIEVE HIGH-GRADE FIBER

ents in the tanks. Located at the inlet end of all the tanks could be flash mixers to insure dispersion of the papers, the return liquid, and the surfactant additions.

The system could be designed for either a batch or continuous operation. Using the batch operation, the tanks would act independently from one another. If the dimensions of the rectangular tanks in this flow diagram are assumed to be 30 feet wide, 100 feet long, and 10 feet deep, recoveries from the tank sumps can be estimated. Based on the results and loading rates calculated for various wetting liquids in this investigation, the required detention times can be estimated and the recovery operations can be discussed for the proposed sequence of wetting steps. The plant can be operated at a rate of 30 tons per day for an equally weighted distribution of the papers. The system will be batch operated with a 3.75 ton load every 3 hours.

The mixed wastepapers should be pretreated by the shredder and air separator to remove contaminants before they are introduced into the first settling tank filled with water. If the tank is equipped with paddle flocculators to provide gentle agitation for approximately 30 minutes to the mixture, 0.83 tons of groundwoods can be removed by the bottom scrapper at the discharge trough after agitation ceases. These recovered groundwoods can be sent directly to a hopper for secondary deinking and pulping. The 2.92 tons of floating papers can be transferred to the second settling tank filled with a dilute cationic surfactant. If the papers are gently stirred with mechanical impellers, 0.33 tons of the bleached bond and 0.73 tons of the bleached kraft can

be recovered at the sump with detention times of approximately 1 hour and 3 hours, respectively. At this time, the 1.86 tons of papers which are still floating can be transferred at the outlet weir to the third tank containing a dilute concentration of an anionic surfactant. The mixture could be gently stirred with air diffusers for periods of 1 and 3 hours to recover 0.29 and 0.80 tons of the light-weight and heavy-weight unbleached kraft papers, respectively. The papers still floating would be the heavily coated foodboards which could be removed using a skimmer and transferred to a hopper for secondary treatment. While other operations could be proposed to treat the mixture to recover different high-grade pulp substitutes, it is felt that this proposed sequence of operations includes the important procedures which should be followed for any recovery arrangement.

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